*Review Article*

# Review on Physicochemical Modification of Biodegradable Plastic: Focus on Agar and Polyvinyl Alcohol (PVA)

## Mezigebu Belay [iD] [1,2]

[1]*Biotechnology Center, Institute of Research and Development, Defense University, Bishoftu 1041, Ethiopia*
[2]*Department of Metallurgical and Materials Engineering, College of Engineering, Defense University, Bishoftu 1041, Ethiopia*

Correspondence should be addressed to Mezigebu Belay; mezgebu.belay@dec.edu.et

Plastics materials which are used in our daily life especially for packaging applications are derived from petrochemicals. Though these plastic materials satisfy the required properties of packaging materials in terms of strength, water resistance, and durability, they are not biodegradable and stay in landfills for plenty of years. This causes serious environmental threat and pollution. Owing to this, biodegradable plastics have been emerged as an alternative to conventional plastics. However, most of the biodegrade plastics are dependent on forest reserves even some may affect food supply. Nevertheless, agar and polyvinyl alcohol (PVA) neither causes deforestation nor affect the food stock. Though agar and PVA neither causes deforestation nor affect the food supply, they have high water absorption and a moderate tensile strength. This restricts the use of these polymers for applications. Researchers have used physicochemical modification methods to improve the properties of biodegradable polymers with due attention of agar and PVA. This review presents the basics of polymers, biodegradable polymers, chemistry of biodegradation, environmental impacts of biodegradable polymers, and the physicochemical modification of biodegradable polymers with a special focus of agar and PVA.

## 1. Introduction

Plastics are ubiquitous and are commonly used in our daily life for different applications such as agriculture, electronics, constructions, garments, and packaging [1]. There is a continuous demand of plastic in industries such as packaging and other sectors [2, 3]. There are 21,000 of plastics facilities in USA [4], the plastic consumption in India is estimated to reach to 20 million ton per annum in 2020, 46 million ton of plastic was used in Europe in 2013, and the world production of plastics in 2013 was reached to 250 million tons per annum (Figure 1) [5]. This shows that there is a high demand of plastic in the globe. They are also extremely important in the job market as well as packaging throughout the world.

Though plastics are used for different applications, around 42% of the plastics are used for packaging applications [6].

Most packaging materials are derived from petrochemicals. Though they satisfy many of the required properties of good packaging materials in terms of strength, water resistance, and durability, they are not biodegradable [7, 8]. Owing to this, they end up in landfills where they stay for hundreds of years and cause serious environmental issues [9–11]. To minimize these problems, bio plastics have emerged rapidly as an alternative to petro-based plastics [12–22]. The main advantage of these kinds of plastics is their biodegradability, sustainability, and ecological responsibility [16, 22, 23]. While bio plastics are biodegradable, ecological responsible, and sustainable, most of them heavily depend on forest reserves and even some may affect food supply for their production. For example, cellulose is extracted from plant sources; bio-amide 11 is derived from vegetable oil and polylactic acid (PLA) is derived from maize and crop, which is a food source. Hence, the use of bio plastics as packaging materials may cause deforestation and
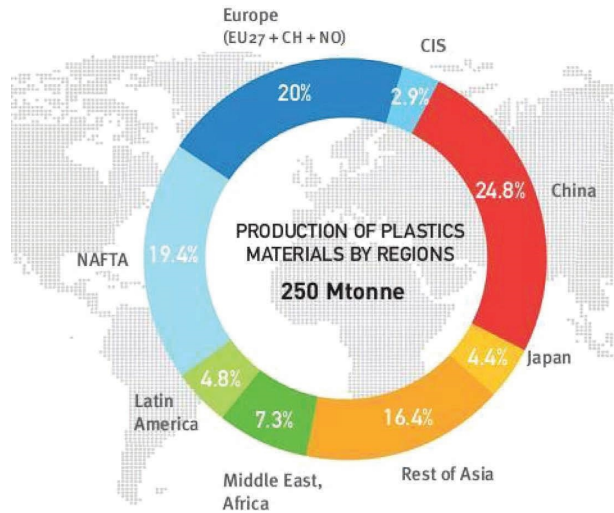
FIGURE 1: Plastic usage. Adapted from reference [5].

scarcity of food resources. For this reason, we choose agar and polyvinyl alcohol (PVA) as our starting materials. Agar is a natural polymer derived from seaweed, and PVA is a synthetic polymer. The motivation to choose agar and PVA is their abundance and that they do not cause deforestation and are not used as food. However, their applicability is limited by their properties, especially moderate strength and high water absorption as compared to petro-based plastics. These properties need tailoring before implementing these materials for packaging applications. As step towards this objective, researchers used physico-chemical methods to improve the properties of biodegradable polymers. In this paper, the basics of polymers, polymers used for packaging applications, biodegrade polymers, chemistry of bio-degradation of biodegradable polymers, source of bio-degradable polymers, and methods used to improve the properties of biodegradable polymers with more focus on agar and PVA are discussed.

*1.1. Polymers.* "Polymer, any class of natural or synthetic substances composed of very large molecules called mac-romolecules that are multiples of simpler chemical units called monomers" [24]. They are organic molecules which comprise repeating carbon-based units. They may contain a single repeating monomer (homopolymer) or two or more monomers (copolymers) and may be amorphous or crys-talline. Most of them contain both amorphous and crys-talline phases. Crystalline polymers are stronger than amorphous polymers due to the difficulty of slippage be-tween the chains. The ability to tailor the physicochemical properties of polymers provides the opportunity to fabricate polymeric materials for versatile applications. This makes them to be versatile class of materials which are found in all areas of engineering. They play important role and become indefensible to our life because of their versatile applications such as packaging, agriculture, consumer products, and pharmaceuticals. Their development and improvement of their properties depend on their application and data ob-tained via rigorous testing. The application and development

of their composite is also continuously and rapidly growing due to their versatile property, abundance, low cost, and ease of manufacturing. Interestingly, polymers are processed to form plastics, rubbers, and fiber materials.

Plastics are natural or synthetic organic resins. They are processed by forming or molding into shapes. They are important engineering materials due to the wide range of properties. They offer versatile properties that are not at-tainable from other materials. Plastics have light weight, wide range of colors, low thermal and electrical conduc-tivities, less brittleness, good toughness, good resistance to acids, high dielectric strength, etc [25]. Owing to these properties, they are used for many applications and become vital in everyday life. Hence, they are the most widely used polymers in our daily life especially for packaging applications.

*1.2. Types of Polymers.* Since polymers have versatile properties, they can be classified on various ways based on their origin, structure, molecular force, polymerization, and biodegradability [26–28] (Table 1). The table given shows types and examples of polymers based on different criteria.

*1.3. Polymers for Packaging Applications.* Packaging repre-sents an important consumption of plastics which have rapidly increased over the past few decades with an annual growth rate of 5% [19]. Around 42% of the plastics used worldwide are used for packaging applications [1]. Among the plastic materials, petroleum plastics such as polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), polyvinyl chloride (PVC), polyamide (PA), polyurethane, and polyester (PS) are widely used for packaging applica-tions. They are very successfully in packaging applications due to their relatively low cost, good strength, stability, and water resistance. However, these plastics are not bio-degradable. As a result, the use of these materials as packaging materials causes serious environmental problems.

*1.4. Biodegradable Polymers.* Polymers form the backbone of plastic materials and continually employed in an expanding many areas particularly in the packaging sector. Most of them are derived from petroleum resources. The annual production of petroleum based plastics exceeded over 300 million ton in 2015 [29]. Petroleum-based synthetic plastics are resistant to biodegradation because their polymer chains are too large and too tightly bonded together to be broken apart and assimilated by microorganisms [25]. This con-sequently causes a problem for waste disposal [30] and become a serious environmental issue. Efforts have been made to reduce the negative impact of plastic waste by incineration and recycling. Nevertheless, incineration yields toxic emissions such as dioxin [31]. In addition, plastic recycling presents a negative eco balance due to the necessity to wash the plastics wastes, as well as the energy con-sumption during the recycling processes [25]. The threat and concern in environmental pollution and global warming drive for the development of bio degradable polymers.

TABLE 1: Types, examples, and classification of polymers on various bases.

| Basis of classification | Polymer type | Example |
|---|---|---|
| Origin [26–28] | Natural | Proteins |
| | | Cellulose |
| | | Starch |
| | Synthetic | Nylon |
| | | Polyethylene |
| | | Polyester |
| | | Teflon |
| | | PVC |
| Structure [26–28] | Linear | Teflon |
| | | Polypropylene |
| | Branched | Starch |
| | | Glycogen |
| | Crosslinked | Melamine |
| Molecular forces [26–28] | Elastomers | Rubber |
| | Fibers | Silk |
| | | Nylon |
| | Thermoplastics | Polyethylene |
| | | Polystyrene |
| | | Polypropylene |
| | Thermosetting | Polyester |
| | | Poly urethane |
| Polymerization [26–28] | Addition | PVC |
| | Condensation | Nylone-66 |
| Biodegradability [26–28] | Non-biodegradable | |
| | Biodegradable | |

Biodegradable polymers are capable of quite readily degradation by hydrolysis into carbon, hydrogen, oxygen, and other biomass by the action of microbial and photo degradation. They can be degraded by the action of microorganisms in both aerobic and anaerobic conditions aided by biotic central reactions such as photo degradation, oxidation, and hydrolysis [22, 32]. These kind of plastics offer many advantages such as increase in soil fertility, low accumulation of bulk materials, reduction in the cost of waste management, and reduction in the emission of greenhouse gases.

*1.5. Environmental Impact of Biodegradable Plastics.* The use of biodegradable plastics has a positive impact on the environment. Biodegradable plastics, after their intended use by the consumers, can be disposed in a bio-waste collection and then composed. The new biomass that is produced is environmental friendly and leaves no toxic residue. In addition, biodegradable materials suited for packaging applications are often used in agricultural products. For example, young plants which are particularly susceptible to frost covered with films such as Ecoflex [33–35]. At the end of the growing season, the films can be broken down to soil by microorganisms, thereby increasing the fertility of the soil.

The constant accumulation of plastic wastes in the environment leads to adverse environmental impacts such as loss of land fertility, harmful health effects on grazing animals, and environmental pollution are main drawbacks of using nonbiodegradable plastics [1]. To overcome these drawbacks, recycling of plastics has been attempted but is much less than required [36]. For example, in the United States only 10% of the plastics are recycled [37]. Energy recovery by the incineration of plastic wastes has been successfully implemented in some countries such as Sweden and USA to get rid of the wastes [38]. However, the process emits $CO_2$ and other toxic gases such as dioxin [7]. For this season, biodegradable polymers become a more sensible choice as they avoid plastic waste accumulation, $CO_2$, and toxic emission and are composted to organic matter. The complete substitution of the conventional plastic with renewable feed stock would lead to a balanced carbon dioxide in the atmosphere [39]. In addition, the requirement for manufacturing biodegradable plastics is less than that of conventional plastic [40]. Hence, biodegradable plastics can result in energy savings than the conventional plastics.

*1.6. Chemistry of Biodegradations.* "Biodegradation is the breakdown of chemicals by microorganisms" [41, 42]. It is the only degradation pathway that can completely remove a polymer or its degradation product from the environment. Firstly, the macromolecule is depolymerized into short chains. This step normally occurs outside the microorganism due to the size of the polymer chain and insoluble nature of many polymers. Secondly, the polymer chains cleavage by extracellular enzyme and biotic reactions. The degradation of polymer depends on the properties of the polymer and the environmental condition: temperature, microorganisms, presence of oxygen, and water [43]. Chemical structure responsible for functional group stability, reactivity, and swelling behavior is the most important factor that controls the biodegradability of polymers [44]. Physico-chemical properties such as molecular weight, porosity, and elasticity are other factors that affect biodegradation of polymers. The biodegradability of polymers can be adversely affected by increase hydrophobicity, macromolecule molecular weight, and size of crystalline domain [45].

The degradation of carboxylic acid derivative polymers such as polylactic acid, polygycolic acid, bio-poly ester (oly-$\beta$-hydroxy-yalkanoates), and polycaprolactone takes place by hydrolysis [46–48]. These polymers contain hydrolytically labile functional groups such as esters and ortho esters. The functional groups are susceptible to hydrolysis [49]. Hence, it can be degraded by hydrolysis. This kind of degradation is fast, and the rate of degradation can be fine-tuned by the proper choice of molecular weight and co-polymerization of monomeric units. On the other hand, the degradation of carbonic acid derivative polymers such as poly (ethylene carbonate) (PEC) and poly (trimethylene) (PTMC) takes place by oxidation [44]. Unlike hydrolysis degradation, this kind of degradation is slow and can be observed in surface cracking and pitting by surface active oxygen species [44, 50]. The rate of biodegradation can be improved initiating by catalytic amounts of oxidizing agents [44].

Despite the type of degradation mechanism, biodegradation can be characterized by bulk erosion and surface erosion. Degradation proceeds throughout the matrix, and sharp drop of molecular weight and retarded mass is

observed in bulk erosion. On the other hand, degradation proceeds exclusively at the surface and a fast onset of weight loss and constant residual molecular weight till complete degradation are observed in surface erosion. Polygycolic acid (PGA) and poly lactic-co-glycolic acid (PLGA) degrades by bulk erosion whereas, polyester and polyanhaydrides degrade by surface erosion [51–56].

*1.7. Sources of Biodegradable Polymers.* Biodegradable polymers can be classified as renewable and nonrenewable based on the origin of the raw materials and the process used in their manufacturing. Biodegradable polymers need not necessarily be based on renewable resources as biodegradability is more dependent on the chemical nature and bonding rather than origin [57]. There are also several biodegradable synthetic carbon-based polymers. Biodegradable polymers can be natural which can be extracted from renewable resources or synthetic which can be obtained from petrochemicals [58] (Figure 2). The natural polymers are extracted from polysaccharides and proteins. Natural Polymers that can be extracted from polysaccharides include cellulose, starch, chitosan, agar, and carrageenan. Natural polymers that can be extracted from proteins include gelatin, gluten, alginate, whey protein, and collagen. Bio based plastics may be biodegradable or not [31, 60, 61]. Unlike natural polymers, synthetic polymers can be synthesized by either microbial production and fermentation or by conventional and chemical synthesis. Polymers that can be obtained by microbial production and fermentation include polyhydroxy-alkanoates (PHA), poly-hydroxybutyrate (PHB), and polyhydroxybutyrate-co-hydroxyvalerate (PHBV). Polymers that are extracted by conventional and chemical synthesis are obtained from biomass or petroleum [59, 62]. Polylactic acid (PLA) is an example of polymer that can be generated by conventional and chemical synthesis from biomass. On the other hand, polyvinyl alcohol (PVA), poly glycolic acid (PGA), Polybutylene succinate adipate (PBSA), and polycaprolactone (PLC) are derived from petroleum products by conventional and chemical synthesis.

*1.8. Agar.* Agar is an unbranched polysaccharide that is extracted from the supporting structure in the cell wall of agrophytae marine algae which belongs to Rhodophyta phylum [63, 64]. It contains a mixture of a linear polysaccharide known as agarose and a heterogeneous mixture called agaropectin [65, 66]. It is used as culture media, vegetable substitute, thickener of soups, desserts, laxatives, an appetite suppressan, etc [67, 68]. The gelling agent of agar is derived from the cell wall of genera Gelidium and Gracilaria. It consists of subunits of galactose. It was first discovered for microbial application by a German microbiologist Walther Hesse and Gr [69]. Agarose make up 70% of the mixture and consists of disaccharide of D-galactose and 3, 6-anydro-L-galactopyronose [70]. Agropectin occurs in lesser amount and contains alternating units of D-galactose and L-galactose. It dissolves at 85°C and solidifies close to human body temperature. This property makes it suitable for scientific incubation over other

solidifying agents which dissolve at the body temperature. It is white and semitranslucent and produces a reversible firm jelly even at lower concentration. It dissolves on heating and resets on cooling. The firmness of the gel is determined by the amount of agar used to create the gel. Due to its good gel forming property, biocompatibility, nontoxicity, and biodegradability, agar becomes an attractive candidate to make films for packaging applications. However, high water absorption, moderate tensile strength, and thermal property restrict its implementation. To improve the previous lacunae, researchers have used methods to improve its properties. The methods that are used to improve its properties are reviewed in the following section.

*1.8.1. Methods Used to Improve the Properties of Agar.* To overcome the limitation of polymers, reinforcement, and chemical crosslinking of agar are used [71–77].

(1) *Reinforcement.* Reinforcement can enhance the mechanical and barrier properties of polymer by the establishment of a composite. A composite is a combination of at least two materials working together to produce a material that has better properties than the constituent phases [78]. In a composite, the constituent phases must be dissimilar and separated by a distinct interface. A better property is tailored by the combination of two or more distinct phases by the principle of this combined action. It consists of a bulk material (the matrix) and reinforcement (filler). The matrix is the continuous phase, and the reinforcement is the dispersed phase. The purpose of the matrix is to transfer the stress to the other phase whereas; the purpose of the reinforcement or filler is to enhance the tensile strength and toughness of the material. The property of the composite is a function of concentration, size, distribution, and the orientation of the reinforcement [79]. When a load is applied on a composite, the force is shared by the matrix and the reinforcement.

$F_C = F_M + F_R$ where $F_C$ is the force on the composite, $F_M$ is the force shared by the matrix, and $F_R$ is the force shared by the reinforcement [79].

$F = \sigma A$ where $F$ is the applied force and $A$ is the cross sectional area. Then,

$\sigma_C A_C = \sigma_M A_M + \sigma_R A_R$, where $\sigma_C$ is the stress on the composite, $A_C$ is cross-sectional area of the composite, $\sigma_M$ is stress on the matrix, $\sigma_R$ the stress of the reinforcement or filler, and is $A_R$ is cross sectional area of the reinforcement or filler.

Dividing both sides of the equation by $Ac$

$$\sigma_c = \frac{\sigma_m A_m}{A_c} + \frac{\sigma_r A_r}{A_c}, \tag{1}$$

where $A_m/A_C$ is the volume fraction of the matrix and $A_r/A_C$ is the volume fraction of the filler. Then,

$$\sigma_c = \sigma_m A_m + \sigma_r A_r, \tag{2}$$

where $V_m$ is the volume fraction of the matrix and $V_r$ is the volume fraction of the filler [79].

If the bonding between the matrix and the filler is good, the matrix and the filer will extend by the same size so that
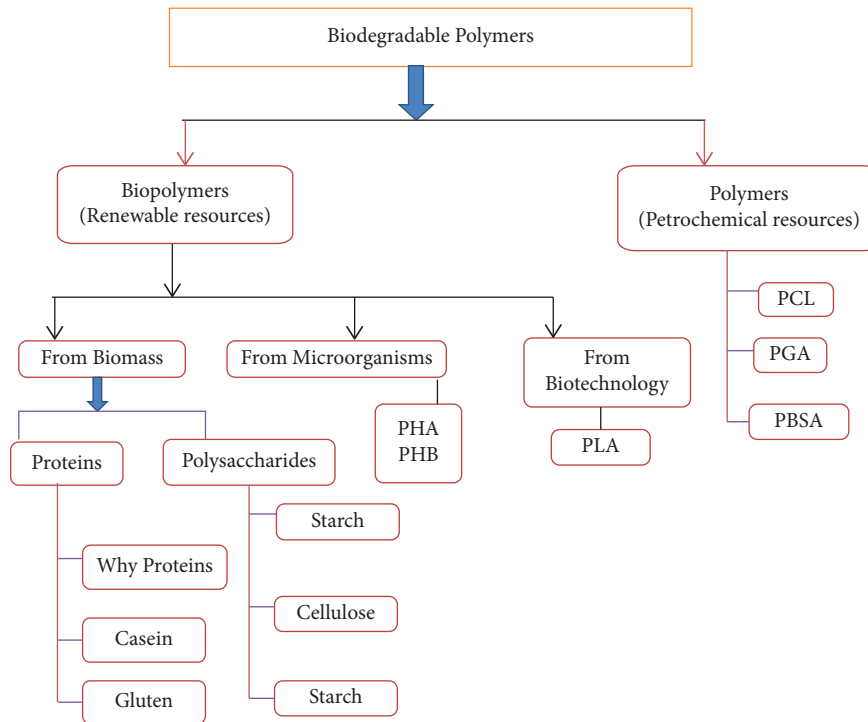
FIGURE 2: Sources of biodegradable polymers. Adapted from [59].

the stain of the matrix and the filler will be equal. Under this condition, we get the following equation:

$$\frac{\sigma_c}{\varepsilon} = \frac{\sigma_m A_m}{\varepsilon} + \frac{\sigma_r A_r}{\varepsilon},\tag{3}$$

where $\sigma_m/\varepsilon$ is Young's modulus of the matrix and $\sigma_r/\varepsilon$ is Young's modulus of the filler. Then,

$$E_c = E_m V_m + E_r V_r,\tag{4}$$

where $E_m$ is Young's modulus of the matrix and $E_r$ is Young's modulus of the filers.

Different researchers have used different reinforcements to improve the properties of agar. For example, Awadhiya et al. [77] showed the change of tensile strength from 25.1 MPa for pure agarose to 60.1 MPa for agarose/bacterial cellulose composite. Shankar et al. [71] reported an improvement of tensile strength from 45.7 MPa for pure agar to 52.1 MPa for lignin/agar composites. Rhim [80] showed an increase in tensile strength of agar from 31 MPa for pure agar to 45 MPa for agar/$\kappa$-carrageenan composites. Belay et al. [81]. reported the preparation and characterization of composite of agar/reduced grapheme oxide (RGO) and agar/graphenee oxide (GO) composites [82]. In the work, the tensile strength of agar was improved from 38.31 MPa for pure agar to 64.94 MPa for RGO/agar composite and 83.69 MPa for GO/agar composites. The water resistance and swelling resistance of agar was also improved after incorporation of RGO and GO which was observed through contact angle and swelling ratio data. However, the thermal stability was slightly improved due to the absence of covalent bonding. In other paper, Belay et al. [83] has reported the synergistic effect of bacterial cellulose reinforcement and

succinic acid crosslinking. In this work, the tensile strength of agar was improved from 55 MPa for pure agar to 86.30 MPa bacterial cellulose/agar composites. Furthermore, the tensile strength of agar was improved from 55 MPa fore agar to 111 MPa for the synergistic effect of bacterial cellulose reinforcement and succinic acid crosslinking.

(2) *Crosslinking.* Crosslinking is interconnecting polymer chain at several points to make macromolecule with a networked structure. The interconnecting points are known as crosslinking points. Crosslinking plays a vital role for the modification of virgin polymers and is used to improve water resistance, strength, and stability [84–89]. Cross linked polymers are used in different fields such as synthesis, extraction, tissue engineering, drug delivery, and biomedical applications [90, 91].

Crosslinking can be classified as in-situ crosslinking and post crosslinking. "In-situ crosslinking is a process of direct crosslinking of monomers with a crosslinker to obtain a macromolecular chain. Whereas, post crosslinking is a process of crosslinking after polymerization of the monomeric units" [92, 93]. In-situ crosslinking proceeds by chain growth and step growth polymerization processes. Post crosslinking between polymeric chains is usually carried out by reaction between the reactive groups on the polymer chains with crosslinkers having reactions with two or more functional groups. Crosslinking reactions are usually initiated by heating or photo irradiation. Polymers can be crosslinked by chemical crosslinking or physical crosslinking. The degree of crosslinking in chemical crosslinking is controlled by amount of crosslinker, crosslinking time, temperature, processing, and initiator/catalyst (type and concentration). Unlike chemical crosslinking, physical

crosslinking is performed using interactions other than the covalent bond such as hydrogen bonding or ionic interaction. Physical crosslinking is weak as compared to chemical crosslinking as the former is formed by secondary forces.

Polymer chains are generally held together by weak Van der Waals force or hydrogen bond and easily slide on each other when pulled by tensile forces. Therefore, crosslinking is employed to restrict the movement of polymer chains.

Crosslinking restricts the relative movement of polymer chains; this reduces the amount of water entering between the chains which lead to the reduction of swelling. In case of agar, the amount of hydroxyl groups get reduced when chemically crosslinked. Awadhiya et al. [87] showed a reduction in water uptake by ~8 fold with tensile strength improvement (25.1 MPa to 52.7 MPa) by crosslinking agarose with citric acid. However, the chain degradation was observed at higher concentration of crosslinkers. Belay et al. [83] showed reduction in water absorption by ~5 fold with tensile strength improvement (55 MPa to 93.40 MPa). Sonket et al. [94] demonstrated the cross linking of agar with aromatic diisocyanate, DDI (4,4 diphenyl diisocyanates and aliphatic diisocyanates), and HDI (1,6 Hexamethylene diisocyanate). In this work, a reduction in water absorption of ~6 fold and ~5 fold was reported with DDI and HDI cross linker, respectively. In addition, the thermal stability of cross linked samples was improved due the presence of covalent linkage.

# 2. PVA

Poly (vinyl alcohol) (PVA) $(CH_2CH(OH))_n$ is a water-soluble, transparent, semicrystalline polymer with excellent mechanical properties, chemical resistance, and biocompatibility [95–97]. It is synthetic biodegradable and hydrophilic polymer which has potential applications.

Poly (vinyl alcohol) (PVA) is synthesized by the hydrolysis of poly (vinyl acetate). Owing to its biocompatibility, transparency, chemical resistance, toughness, nontoxicity, water solubility, and excellent film forming properties, PVA finds application in but not limited to packaging, paper industry, plywood manufacturing, as pressure-sensitive adhesives, textile sizing, membranes, water soluble photo resists, and biomedical materials [89, 98–102]. The properties of PVA depend on the molecular weight, as well as the degree of hydrolysis and polymerization condition of the parent poly (vinyl acetate) monomer [88]. Increase in hydrolysis improves the degree of crystallinity and molecular mobility of PVA films, whereas increase in molecular weight decreases its crystallinity and mobility [103].

## 2.1. Methods Used to Improve the Properties of PVA

*2.1.1. Reinforcement of PVA.* Different researchers showed the role of reinforcement on the tensile strength of virgin PVA. For example, Yang et al. [104] reported a change of tensile strength from 22 MPa for pure PVA to 29 MPa for PVA/graphene composite, an increase of 32%, for their layer aligned polyvinyl alcohol/graphene composite. Jiang et al. [105] showed improvement of tensile strength from 23 MPa for pure PVA to 49.5 MPa for polyvinyl alcohol/graphene composite. In addition, they also reported an increase in the thermal stability of PVA. The peak temperature of the polyvinyl alcohol/graphene composite increased by about 8°C compared to that of pure PVA. The improvement in thermal stability was due to the hydrogen bonding interaction between the residual oxygen containing groups of graphene oxide and hydroxyl group of PVA. Zhao et al. [106] reported 150% improvement of tensile strength, and nearly 10 times improvement of Young's modulus in PVA-graphene composites. Liang et al. [107] reported 76% improvement in tensile strength from 49.9 MPa for pure PVA to 87.6 MPa for PVA-graphene composite, and 62% increment in Young's modulus from 2.13 to 3.45 GPa. Xu et al. [108] reported the improvement of tensile strength from 65 MPa to 110 MPa and Young's modulus from 2.1 to 4.8 GPa for graphene oxide/PVA composite. Belay et al. [81] showed an increase of tensile strength from 31.19 MPa for pure PVA to 81.63, 104.6, and 106.73 for PVA with grapheme oxide (GO) reinforcement, synergistic effect of GO reinforcement with AdA crosslinking, and synergistic effect of GO reinforcement with SuA cross linking, respectively.

*2.1.2. Crosslinking of PVA.* The solubility of PVA in water allows fabrication of solution cast films without the use of organic solvent. However, high water absorption during usage is not desirable. Besides, its moderate strength and thermal stability further limit its application. Absorption of water, due to large number of -OH groups, results in swelling that further deteriorates the strength of PVA by reducing its interchain interactions [109, 110].

Hence, reduction in water absorption (swelling) of PVA is desirable upon its exposure to water. In addition, PVA must maintain its strength even after exposure to water to hold the packaged goods.

To lower water absorption (swelling) characteristics of PVA, it is chemically crosslinked using chemicals such as dialdehydes [111–116], dicarboxylic [86, 117–121] or tricarboxylic acids [102, 122], diisocyanates [88], boric acid [123], and organosilanes [124, 125]. The crosslinker not only reduces the number of -OH by reacting with them but also restricts the movement of PVA chains led by the incoming water molecules thus preventing swelling. In addition, crosslinking improves the strength of PVA [86, 88, 119].

Krumova et al. [88] showed the crosslinking of PVA with hexamethylene isocyanetes via the formation of urethane bond. Figueiredo et al. [126] crosslinked PVA with glutaraldehyde and showed the improvement of water resistance and thermal stability of PVA.

Heydari [119] crosslinked PVA membrane with fumaric acid at 150°C for three different time of 10, 30, and 60 minutes, and investigated the effect of crosslinking time on thermal, mechanical, and water absorption property. They reported the improvement of thermal stability and

water uptake with increased crosslinking duration. However, they observed a decrease in the tensile strength beyond 10 minutes crosslinking time.

Sonker et al. [127] cross linked PVA with two different acids; suberic acid (aliphatic) and terephthalic acid (aromatic), and investigated the effect of crosslinker geometry on the swelling, thermal, and mechanical properties of PVA. In this report, no significance change was observed in the swelling of PVA due to difference in the crosslinker geometry. The tensile strength and crystallinity of PVA was increased in suberic acid (aliphatic) crosslinked PVA, which was not the case in terephthalic acid (aromatic) cross linked PVA. However, in swelling and thermal properties of crosslinked samples, no role of crosslinker shape was observed. It was due to crosslinking densities values, which was found similar in suberic acid and terephthalic acid crosslinked PVA. Belay et al. [81] showed an increase of tensile strength from 31.19 MPa for pure PVA to 63.93, 72.69, 104.6, and 106.73 for PVA with AdA crosslinker, PVA with SuA crosslinker, synergistic effect of GO reinforcement with AdA crosslinking, and synergistic effect of GO reinforcement with SuA cross linking, respectively.

## 3. Conclusion

The conventional plastics that are used for packaging applications are not biodegrade. As a result, they end up in landfills. This cause serious pollution and threat to the environment. To surmount this issue, biodegradable plastics have emerged as alternatives to conventional plastics. The main advantage of biodegradable plastic is their biodegradability, sustainability, and ecological responsibility. Though biodegradable plastics are biodegradable, sustainable, and ecological responsible, most of them are dependent on forest reserves even some may affect food supply. This necessitates searching other alternatives which neither causes deforestation nor affect food supply. Agar and PVA neither causes deforestation nor affect food supply. However, they have high water absorptions and moderate tensile strength to be used for packaging applications. Different researchers have used physic-chemical methods which are used to improve the properties of agar and PVA. This paper reviews the physic-chemical methods used to improve the properties of these polymers. The review shows that crosslinking basically reduces water absorption with the improvement of tensile strength, reinforcement improves tensile strength, and synergistic effect of the two further enhances tensile strength due to interfacial binding between the filler and the matrix.

## Data Availability

The data used to support the findings of this study are available from the authors upon reasonable request.

## Conflicts of Interest

The author declares that there are no conflicts of interest.

## References

[1] A. Okunola A, O. Kehinde I, A. Oluwaseun, and A. Olufiropo E, "Public and environmental health effects of plastic wastes disposal: a review," *Journal of Toxicology and Risk Assessment*, vol. 5, no. 2, 2019.

[2] A. L. Andrady and M. A. Neal, "Applications and societal benefits of plastics," *Philosophical Transactions of the Royal Society B: Biological Sciences*, vol. 364, no. 1526, pp. 1977–1984, 2009.

[3] A. Sangroniz, J. B. Zhu, X. Tang, A. Etxeberria, E. Y. X. Chen, and H. Sardon, "Packaging materials with desired mechanical and barrier properties and full chemical recyclability," *Nature Communications*, vol. 10, no. 1, p. 3559, 2019.

[4] S. Berkesch, *Biodegradable Polymers*, A Rebirth of Plasti Michigan State University March, Michigan, USA, 2005.

[5] Plastic Europe, "Plastics – the Facts 2014/2015 an analysis of European plastics production, demand and waste data," 2017, https://www.plasticseurope.org/application/files/5515/1689/9220/2014plastics_the_facts_PubFeb2015.pdf.

[6] C. Silvestre, D. Duraccio, and S. Cimmino, "Food packaging based on polymer nanomaterials," *Progress in Polymer Science*, vol. 36, no. 12, pp. 1766–1782, 2011.

[7] R. Verma, K. Vinoda, M. Papireddy, and A. Gowda, "Toxic pollutants from plastic waste- A review," *Procedia Environmental Sciences*, vol. 35, pp. 701–708, 2016.

[8] S. M. Emadian, T. T. Onay, and B. Demirel, "Biodegradation of bioplastics in natural environments," *Waste Management*, vol. 59, pp. 526–536, 2017.

[9] D. K. A. Barnes, F. Galgani, R. C. Thompson, and M. Barlaz, "Accumulation and fragmentation of plastic debris in global environments," *Philosophical Transactions of the Royal Society B: Biological Sciences*, vol. 364, no. 1526, pp. 1985–1998, 2009.

[10] J. Hopewell, R. Dvorak, and E. Kosior, "Plastics recycling: challenges and opportunities," *Philosophical Transactions of the Royal Society B: Biological Sciences*, vol. 364, no. 1526, pp. 2115–2126, 2009.

[11] E. Pongrácz, *The Environmental Impacts of Packaging*, Foodprint, Okkiam, Thoraipakkam, India, 2007.

[12] Y. Lu, L. Tighzert, F. Berzin, and S. Rondot, "Innovative plasticized starch films modified with waterborne polyurethane from renewable resources," *Carbohydrate Polymers*, vol. 61, no. 2, pp. 174–182, 2005.

[13] S. Z. Rogovina, "Biodegradable polymer composites based on synthetic and natural polymers of various classes," *Polymer Science - Series A C*, vol. 58, no. 1, pp. 62–73, 2016.

[14] J. K. Pandey, A. P. Kumar, M. Misra, A. K. Mohanty, L. T. Drzal, and R. Palsingh, "Recent advances in biodegradable nanocomposites," *Journal of Nanoscience and Nanotechnology*, vol. 5, no. 4, pp. 497–526, 2005.

[15] J. W. Rhim and P. K. W. Ng, "Natural biopolymer-based nanocomposite films for packaging applications," *Critical Reviews in Food Science and Nutrition*, vol. 47, no. 4, pp. 411–433, 2007.

[16] A. Sorrentino, G. Gorrasi, and V. Vittoria, "Potential perspectives of bio-nanocomposites for food packaging applications," *Trends in Food Science & Technology*, vol. 18, no. 2, pp. 84–95, 2007.

[17] P. Bordes, E. Pollet, and L. Avérous, "Nano-biocomposites: biodegradable polyester/nanoclay systems," *Progress in Polymer Science*, vol. 34, no. 2, pp. 125–155, 2009.

[18] C. J. Weber, V. Haugaard, R. Festersen, and G. Bertelsen, "Production and applications of biobased packaging materials for the food industry," *Food Additives & Contaminants*, vol. 19, no. 1, pp. 172–177, 2002.

[19] V. Siracusa, P. Rocculi, S. Romani, and M. D. Rosa, "Biodegradable polymers for food packaging: a review," *Trends in Food Science & Technology*, vol. 19, no. 12, pp. 634–643, 2008.

[20] P. M. Shah, "Edible polymers: challenges and opportunities," *Journal of Polymers*, vol. 2014, Article ID 427259, 13 pages, 2014.

[21] J. W. Rhim, H. M. Park, and C. S. Ha, "Bio-nanocomposites for food packaging applications," *Progress in Polymer Science*, vol. 38, no. 10–11, pp. 1629–1652, 2013.

[22] X. Z. Tang, P. Kumar, S. Alavi, and K. P. Sandeep, "Recent advances in biopolymers and biopolymer-based nanocomposites for food packaging materials," *Critical Reviews in Food Science and Nutrition*, vol. 52, no. 5, pp. 426–442, 2012.

[23] K. G. Harding, T. Gounden, and S. Pretorius, "*Biodegradable*" plastics: a Myth of marketing?" *Procedia Manufacturing*, vol. 7, pp. 106–110, 2017.

[24] S. Heinemann, "Chapter 1 - polymer-based matrix composites," in *Handbook of Nanoceramic and Nanocomposite Coatings and Materials*, pp. 3–27, Butterworth-Heinemann, Oxford, UK, 2015.

[25] Y. Xu, C. Yin, W. Yue, and N. Y. Zhou, "[Microbial degradation of petroleum-based plastics]," *Sheng Wu Gong Cheng Xue Bao*, vol. 35, no. 11, pp. 2092–2103, 2019.

[26] P. Majumder, "The 5 most important classification of polymers," 2018, https://www.sciencedirect.com/science/article/pii/S0008884604002133.

[27] Cebr, "The future potential economic impacts of a bioplastics industry in the UK," A report for the Bio-based and Biodegradable Industries Association, CEBR, London, UK, 2015.

[28] Madhusha, "Difference between branched polymer and linear polyme," 2018, http://pediaa.com/difference-between-branched-polymer-and-linear-polymer.

[29] T. Mekonnen, P. Mussone, H. Khalil, and D. Bressler, "Progress in bio-based plastics and plasticizing modifications," *Journal of Materials Chemistry*, vol. 1, no. 43, pp. 13379–13398, 2013.

[30] M. Avella, J. J. De Vlieger, M. E. Errico, S. Fischer, P. Vacca, and M. G. Volpe, "Biodegradable starch/clay nanocomposite films for food packaging applications," *Food Chemistry*, vol. 93, no. 3, pp. 467–474, 2005.

[31] R. K. Gilpin, D. J. Wagel, and J. G. Solch, "Production, distribution, and fate of polychlorinated dibenzo-p-dioxins, dibenzofurans, and related organohalogens in the environment," in *Dioxins and Health*, pp. 55–87, John Wiley & Sons Inc, New York,NY, USA, 2005.

[32] J. P. Eubeler, S. Zok, M. Bernhard, and T. P. Knepper, "Environmental biodegradation of synthetic polymers I. Test methodologies and procedures," *TrAC, Trends in Analytical Chemistry*, vol. 28, no. 9, pp. 1057–1072, 2009.

[33] M. Malinoconico, *Soil Degradation Bioplastics for Sustainable Modern Agriculture*, M. Malinoconico, Ed., Springer, Cham, 2017.

[34] I. Vroman and L. Tighzert, "Biodegradable polymers," *Materials*, vol. 2, no. 2, pp. 307–344, 2009.

[35] R. Smith, *Biodegradable Polymers for Industraial Applications*, R. Smith, Ed., Wood Head, Cambridge, UK, 2005.

[36] G. Atiwesh, A. Mikhael, C. C. Parrish, J. Banoub, and T. A. T. Le, "Environmental impact of bioplastic use: a review," *Heliyon*, vol. 7, no. 9, Article ID e07918, 2021.

[37] E. Chiellini, P. Cinelli, S. H. Imam, and L. Mao, "Composite films based on biorelated agro-industrial waste and poly(vinyl alcohol). Preparation and mechanical properties characterization," *Biomacromolecules*, vol. 2, no. 3, pp. 1029–1037, 2001.

[38] A. AlabiOkunola, "Public and environmental health effects of plastic wastes disposal: a review," *Journal of Toxicology and Risk Assessment*, vol. 5, 2019.

[39] B. Dahlke, H. Larbig, H. D. Scherzer, and R. Poltrock, "Natural fiber reinforced foams based on renewable resources for automotive interior applications," *Journal of Cellular Plastics*, vol. 34, no. 4, pp. 361–379, 1998.

[40] T. Blog, "7 advantages and disadvantages of biodegradable plastics," *Procedia CIRP*, Aqua Solution Blog, Wellington, The Newzeland.

[41] C. I. Betton, "Lubricants and their environmental impact," in *Chemistry and Technology of Lubricants*, R. M. Mortier, M. F. Fox, and S. T. Orszulik, Eds., pp. 435–457, Springer, Dordrecht, The Netherlands, 2010.

[42] N. Lucas, C. Bienaime, C. Belloy, M. Queneudec, F. Silvestre, and J. E. Nava-Saucedo, "Polymer biodegradation: mechanisms and estimation techniques – a review," *Chemosphere*, vol. 73, no. 4, pp. 429–442, 2008.

[43] R. Mohee and G. Unmar, "Determining biodegradability of plastic materials under controlled and natural composting environments," *Waste Management*, vol. 27, no. 11, pp. 1486–1493, 2007.

[44] M. Acemoglu, "Chemistry of polymer biodegradation and implications on parenteral drug delivery," *International Journal of Pharmaceutics*, vol. 277, no. 1-2, pp. 133–139, 2004.

[45] A. Samir, F. H. Ashour, A. A. A. Hakim, and M. Bassyouni, "Recent advances in biodegradable polymers for sustainable applications," *Npj Materials Degradation*, vol. 6, no. 1, p. 68, 2022.

[46] J. C. Middleton and A. J. Tipton, "Synthetic biodegradable polymers as orthopedic devices," *Biomaterials*, vol. 21, no. 23, pp. 2335–2346, 2000.

[47] K. Schwach-Abdellaoui, J. Heller, and R. Gurny, "Hydrolysis and erosion studies of autocatalyzed poly(ortho esters) containing Lactoyl–Lactyl acid dimers," *Macromolecules*, vol. 32, no. 2, pp. 301–307, 1999.

[48] E. Yasa and K. Ersoy, "Dimensional accuracy and mechanical properties of chopped carbon reinforced polymers produced by material extrusion additive manufacturing," *Materials*, vol. 12, no. 23, p. 3885, 2019.

[49] S. J. Huang, "21 - biodegradation," in *Comprehensive Polymer Science and Supplements*, G. Allen and J. C. Bevington, Eds., pp. 597–606, Pergamon, Amsterdam, The Netherland, 1989.

[50] S. J. McCarthy, G. F. Meijs, N. Mitchell et al., "In-vivo degradation of polyurethanes: transmission-FTIR microscopic characterization of polyurethanes sectioned by cryomicrotomy," *Biomaterials*, vol. 18, no. 21, pp. 1387–1409, 1997.

[51] A. Göpferich, "Mechanisms of polymer degradation and erosion," *Biomaterials*, vol. 17, no. 2, pp. 103–114, 1996.

[52] H. K. Makadia and S. J. Siegel, "Poly lactic-co-glycolic acid (PLGA) as biodegradable controlled drug delivery carrier," *Polymers*, vol. 3, no. 3, pp. 1377–1397, 2011.

[53] S. Lyu and D. Untereker, "Degradability of polymers for implantable biomedical devices," *International Journal of Molecular Sciences*, vol. 10, no. 9, pp. 4033–4065, 2009.

[54] D. S. Katti, S. Lakshmi, R. Langer, and C. Laurencin, "Toxicity, biodegradation and elimination of poly-anhydrides," *Advanced Drug Delivery Reviews*, vol. 54, no. 7, pp. 933–961, 2002.

[55] J. Park, M. Ye, and K. Park, "Biodegradable polymers for microencapsulation of drugs," *Molecules*, vol. 10, no. 1, pp. 146–161, 2005.

[56] A. Göpferich and J. Tessmar, "Polyanhydride degradation and erosion," *Advanced Drug Delivery Reviews*, vol. 54, no. 7, pp. 911–931, 2002.

[57] S. Sinha Ray and M. Bousmina, "3 - biodegradable polymer/layered silicate nanocomposites," in *Polymer Nano-composites*, Y.-W. Mai and Z.-Z. Yu, Eds., pp. 57–129, Woodhead Publishing, NewYork. NY, USA, 2006.

[58] L. Avérous and E. Pollet, "Biodegradable polymers," in *Environmental Silicate Nano-Biocomposites*, L. Avérous and E. Pollet, Eds., pp. 13–39, Springer London, London, UK, 2012.

[59] N.-A. A. B. Taib, M. R. Rahman, D. Huda et al., "A review on poly lactic acid (PLA) as a biodegradable polymer," *Polymer Bulletin*, vol. 80, no. 2, pp. 1179–1213, 2023.

[60] A. Steinbüchel, "Non-biodegradable biopolymers from renewable resources: perspectives and impacts," *Current Opinion in Biotechnology*, vol. 16, no. 6, pp. 607–613, 2005.

[61] M. Oever, *Bio-based and Biodegradable Plastics: Facts and Figures: Focus on Food Packaging in the Netherlands*, Wageningen Food & Biobased Research, Wageningen, The Netherlands, 2017.

[62] M. Adsul, D. K. Tuli, P. K. Annamalai, D. Depan, and S. Shankar, "Polymers from biomass: characterization, modification, degradation, and applications," *International Journal of Polymer Science*, vol. 2016, Article ID 1857297, 2 pages, 2016.

[63] A. Davidson and T. Jaine, *The Oxford Companion to Food*, Oxford reference, oxford, UK.

[64] G. O. Phillips and P. A. Williams, "Handbook of hydrocolloids," 2000, http://www.foodnetbase.com/books/821/contents.pdf.

[65] Y. Tsuchiya and K. C. Hong, "Agarose and agaropectin in gelidium and gracilaria agar," in *Proceedings of the Fifth International Seaweed Symposium*, pp. 315–321, Pergamon, Halifax, August 1965.

[66] A. Nissinovitch, "Chapter 1 - agar," in *Hydrocolloid Applications: Gum Techenology in Food and Other Techenology* p. 6, Chapman & Hall, London, UK, 1997.

[67] Fitday, "Three uses of agar," 2018, https://www.fitday.com/fitness-articles/nutrition/healthy-eating/3-uses-of-agar.html.

[68] Nutrients review.com, "Agar-agar," 2016, http://www.nutrientsreview.com/carbs/soluble-fiber-agar.html.

[69] W. Hesse and D. H. M. Gr, "Walther and Angelina Hesse-Early Contributors to Bacteriology in an unassuming way,. they moved agar from the kitchen to the lab," *Revolutionizing bacteriology*, 1992.

[70] M. Zeece, "Chapter seven - food additives," in *Introduction to the Chemistry of Food*, M. Zeece, Ed., pp. 251–311, Academic Press, Cambridge, MA, USA, 2020.

[71] S. Shankar, J. P. Reddy, and J.-W. Rhim, "Effect of lignin on water vapor barrier, mechanical, and structural properties of agar/lignin composite films," *International Journal of Biological Macromolecules*, vol. 81, pp. 267–273, 2015.

[72] A. Orsuwan, S. Shankar, L. F. Wang, R. Sothornvit, and J. W. Rhim, "Preparation of antimicrobial agar/banana powder blend films reinforced with silver nanoparticles," *Food Hydrocolloids*, vol. 60, pp. 476–485, 2016.

[73] S. Shankar and J.-W. Rhim, "Preparation of nanocellulose from micro-crystalline cellulose: the effect on the performance and properties of agar-based composite films," *Carbohydrate Polymers*, vol. 135, pp. 18–26, 2016.

[74] J. W. Rhim, L. F. Wang, and S. I. Hong, "Preparation and characterization of agar/silver nanoparticles composite films with antimicrobial activity," *Food Hydrocolloids*, vol. 33, no. 2, pp. 327–335, 2013.

[75] J.-W. Rhim, "Effect of clay contents on mechanical and water vapor barrier properties of agar-based nanocomposite films," *Carbohydrate Polymers*, vol. 86, no. 2, pp. 691–699, 2011.

[76] M. Atef, M. Rezaei, and R. Behrooz, "Preparation and characterization agar-based nanocomposite film reinforced by nanocrystalline cellulose," *International Journal of Biological Macromolecules*, vol. 70, pp. 537–544, 2014.

[77] A. Awadhiya, D. Kumar, K. Rathore, B. Fatma, and V. Verma, "Synthesis and characterization of agar-ose–bacterial cellulose biodegradable composites," *Polymer Bulletin*, vol. 74, no. 7, pp. 2887–2903, 2016.

[78] D. V. Rosato, "An overview of composites," in *Handbook of Composites*, G. Lubin, Ed., pp. 1–14, Springer US, Boston, MA, USA, 1982.

[79] W. D. Callister and D. G. Rethwisch, *Materials Science and Engineering: An Introduction* Wiley, Hoboken, NJ, USA, 2014.

[80] J.-W. Rhim, "Physical-mechanical properties of agar/κ-carrageenan blend film and derived clay nanocomposite film," *Journal of Food Science*, vol. 77, no. 12, pp. N66–N73, 2012.

[81] M. Belay, A. K. Sonker, R. K. Nagarale, and V. Verma, "Synergistic strengthening of composite films by crosslinking graphene oxide reinforcement and poly(vinyl alcohol) with dicarboxylic acids: synergistic strengthening of GO-PVA composite films," *Polymer International*, vol. 66, no. 12, pp. 1737–1746, 2017.

[82] M. Belay, R. Nagarale, and V. Verma, "Preparation and characterization of graphene-agar and graphene oxide-agar composites," *Journal of Applied Polymer Science*, vol. 134, no. 33, Article ID 45085, 2017.

[83] M. Belay, S. Tyeb, K. Rathore, M. Kumar, and V. Verma, "Synergistic effect of bacterial cellulose reinforcement and succinic acid crosslinking on the properties of agar," *International Journal of Biological Macromolecules*, vol. 165, pp. 3115–3122, 2020.

[84] H. Soni and A. K. Singhai, "Formulation and development of hydrogel based system for effective delivery of rutin," *International Journal of Applied Pharmaceutics*, vol. 5, pp. 5–13, 2013.

[85] E. M. Ahmed, "Hydrogel: preparation, characterization, and applications: a review," *Journal of Advanced Research*, vol. 6, no. 2, pp. 105–121, 2015.

[86] A. K. Sonker, N. Tiwari, R. K. Nagarale, and V. Verma, "Synergistic effect of cellulose nanowhiskers reinforcement and dicarboxylic acids crosslinking towards polyvinyl alcohol properties," *Journal of Polymer Science Part A: Polymer Chemistry*, vol. 54, no. 16, pp. 2515–2525, 2016.

[87] A. Awadhiya, D. Kumar, and V. Verma, "Crosslinking of agarose bioplastic using citric acid," *Carbohydrate Polymers*, vol. 151, pp. 60–67, 2016.

[88] M. Krumova, D. López, R. Benavente, C. Mijangos, and J. Pereña, "Effect of crosslinking on the mechanical and thermal properties of poly(vinyl alcohol)," *Polymer*, vol. 41, no. 26, pp. 9265–9272, 2000.

[89] V. Giménez, A. Mantecón, and V. Cádiz, "Modification of poly(vinyl alcohol) with acid chlorides and crosslinking with difunctional hardeners," *Journal of Polymer Science Part A: Polymer Chemistry*, vol. 34, no. 6, pp. 925–934, 1996.

[90] A. M. Telford, M. James, L. Meagher, and C. Neto, "Thermally cross-linked PNVP films as antifouling coatings for biomedical applications," *ACS Applied Materials & Interfaces*, vol. 2, no. 8, pp. 2399–2408, 2010.

[91] M. Wu and X. Zhu, "β-Cyclodextrin cross-linked polymer as solid-phase extraction material coupled with the spectrophotometric method for the analysis of serum albumin," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 77, no. 5, pp. 1021–1024, 2010.

[92] S. Mane, *Effect of Chemical Crosslinking on Properties of Polymer Microbeads: Review*, vol. 3, pp. 473–485, 2016.

[93] T. Oyama, "Cross-linked polymer synthesis," in *Encyclopedia of Polymeric Nanomaterials*, S. Kobayashi and K. Müllen, Eds., pp. 1–11, Springer, Berlin, Germany, 2021.

[94] A. K. Sonker, M. Belay, K. Rathore et al., "Crosslinking of agar by diisocyanates," *Carbohydrate Polymers*, vol. 202, pp. 454–460, 2018.

[95] E. Rynkowska, Fatyeyeva, Marais, Kujawa, and Kujawski, "Chemically and thermally crosslinked PVA-based membranes: effect on swelling and transport behavior," *Polymers*, vol. 11, no. 11, p. 1799, 2019.

[96] T. S. Gaaz, A. Sulong, M. Akhtar, A. Kadhum, A. Mohamad, and A. Al-Amiery, "Properties and applications of polyvinyl alcohol, halloysite nanotubes and their nanocomposites," *Molecules*, vol. 20, no. 12, Article ID 22833, 47 pages, 2015.

[97] N. Jain, V. K. Singh, and S. Chauhan, "A review on mechanical and water absorption properties of polyvinyl alcohol based composites/films," *Journal of the Mechanical Behavior of Materials*, vol. 26, no. 5-6, pp. 213–222, 2017.

[98] J. Chen, Y. Li, Y. Zhang, and Y. Zhu, "Preparation and characterization of graphene oxide reinforced PVA film with boric acid as crosslinker," *Journal of Applied Polymer Science*, vol. 132, no. 22, 2015.

[99] S. Tripathi, G. K. Mehrotra, and P. K. Dutta, "Physicochemical and bioactivity of cross-linked chitosan–PVA film for food packaging applications," *International Journal of Biological Macromolecules*, vol. 45, no. 4, pp. 372–376, 2009.

[100] S. Yang, S. Yoo, J. Lee, J. Kim, and J. Yeum, "Surface properties of a novel poly(vinyl alcohol) film prepared by heterogeneous saponification of poly(vinyl acetate) film," *Polymers*, vol. 9, no. 12, p. 493, 2017.

[101] K. Ichimura, "Preparation of water-soluble photoresist derived from poly(vinyl alcohol)," *Journal of Polymer Science - Polymer Chemistry Edition*, vol. 20, no. 6, pp. 1411–1417, 1982.

[102] M. Tsuda, H. Tanaka, H. Tagami, and F. Hori, "SCHOTTEN-BAUMANN esterification of poly(vinyl alcohol). III. Preparation of some photosensitive polymers and the effects of surface active agents on the interfacial esterification," *Makromolekulare Chemie*, vol. 167, no. 1, pp. 183–190, 1973.

[103] M. Hdidar, S. Chouikhi, A. Fattoum, and M. Arous, "Effect of hydrolysis degree and mass molecular weight on the structure and properties of PVA films," *Ionics*, vol. 23, no. 11, pp. 3125–3135, 2017.

[104] X. Yang, L. Li, S. Shang, and X. Tao, "Synthesis and characterization of layer-aligned poly(vinyl alcohol)/graphene nanocomposites," *Polymer*, vol. 51, no. 15, pp. 3431–3435, 2010.

[105] L. Jiang, X. P. Shen, J. L. Wu, and K. C. Shen, "Preparation and characterization of graphene/poly(vinyl alcohol) nanocomposites," *Journal of Applied Polymer Science*, vol. 118, no. 1, pp. 275–279, 2010.

[106] X. Zhao, Q. Zhang, D. Chen, and P. Lu, "Enhanced mechanical properties of graphene-based poly(vinyl alcohol) composites," *Macromolecules*, vol. 43, no. 5, pp. 2357–2363, 2010.

[107] J. Liang, Y. Huang, L. Zhang et al., "Molecular-level dispersion of graphene into poly(vinyl alcohol) and effective reinforcement of their nanocomposites," *Advanced Functional Materials*, vol. 19, no. 14, pp. 2297–2302, 2009.

[108] Y. Xu, W. Hong, H. Bai, C. Li, and G. Shi, "Strong and ductile poly(vinyl alcohol)/graphene oxide composite films with a layered structure," *Carbon*, vol. 47, no. 15, pp. 3538–3543, 2009.

[109] M. V. Konidari, K. G. Papadokostaki, and M. Sanopoulou, "Moisture-induced effects on the tensile mechanical properties and glass-transition temperature of poly(vinyl alcohol) films," *Journal of Applied Polymer Science*, vol. 120, no. 6, pp. 3381–3386, 2011.

[110] M. S. Peresin, Y. Habibi, A. H. Vesterinen, O. J. Rojas, J. J. Pawlak, and J. V. Seppälä, "Effect of moisture on electrospun nanofiber composites of poly(vinyl alcohol) and cellulose nanocrystals," *Biomacromolecules*, vol. 11, no. 9, pp. 2471–2477, 2010.

[111] C. K. Yeom and R. Y. M. Huang, "Pervaporation separation of aqueous mixtures using crosslinked poly(vinyl alcohol), I. Characterization of the reaction between PVA and amic acid," *Angewandte Makromolekulare Chemie*, vol. 184, no. 1, pp. 27–40, 1991.

[112] H. S. Mansur, C. M. Sadahira, A. N. Souza, and A. A. Mansur, "FTIR spectroscopy characterization of poly (vinyl alcohol) hydrogel with different hydrolysis degree and chemically crosslinked with glutaraldehyde," *Materials Science and Engineering: C*, vol. 28, no. 4, pp. 539–548, 2008.

[113] B. Gebben, H. W. van den Berg, D. Bargeman, and C. A. Smolders, "Intramolecular crosslinking of poly(vinyl alcohol)," *Polymer*, vol. 26, no. 11, pp. 1737–1740, 1985.

[114] E. S. Costa-Júnior, E. F. Barbosa-Stancioli, A. A. Mansur, W. L. Vasconcelos, and H. S. Mansur, "Preparation and characterization of chitosan/poly(vinyl alcohol) chemically crosslinked blends for biomedical applications," *Carbohydrate Polymers*, vol. 76, no. 3, pp. 472–481, 2009.

[115] B. Bolto, T. Tran, M. Hoang, and Z. Xie, "Crosslinked poly(vinyl alcohol) membranes," *Progress in Polymer Science*, vol. 34, no. 9, pp. 969–981, 2009.

[116] A. L. Ahmad, N. M. Yusuf, and B. S. Ooi, "Preparation and modification of poly (vinyl) alcohol membrane: effect of crosslinking time towards its morphology," *Desalination*, vol. 287, pp. 35–40, 2012.

[117] S. Jian and S. Xiao Ming, "Crosslinked PVA-PS thin-film composite membrane for reverse osmosis," *Desalination*, vol. 62, pp. 395–403, 1987.

[118] J. M. Gohil, A. Bhattacharya, and P. Ray, "Studies on the crosslinking of poly (vinyl alcohol)," *Journal of Polymer Research*, vol. 13, no. 2, pp. 161–169, 2006.

[119] M. Heydari, "Effect of cross-linking time on the thermal and mechanical properties and pervaporation performance of poly(vinyl alcohol) membrane cross-linked with fumaric acid used for dehydration of isopropanol," *Journal of Applied Polymer Science*, vol. 128, no. 3, pp. 1640–1651, 2013.

[120] J.-W. Rhim, H. Park, C. Lee, J. Jun, D. Kim, and Y. Lee, "Crosslinked poly(vinyl alcohol) membranes containing sulfonic acid group: proton and methanol transport through membranes," *Journal of Membrane Science*, vol. 238, no. 1–2, pp. 143–151, 2004.

[121] N. Işıklan and O. Şanlı, "Separation characteristics of acetic acid–water mixtures by pervaporation using poly(vinyl alcohol) membranes modified with malic acid," *Chemical Engineering and Processing: Process Intensification*, vol. 44, no. 9, pp. 1019–1027, 2005.

[122] D. S. Dlamini, J. Wang, A. K. Mishra, B. B. Mamba, and E. M. V. Hoek, "Effect of cross-linking agent chemistry and coating conditions on physical, chemical, and separation properties of PVA-psf composite membranes," *Separation Science and Technology*, vol. 49, no. 1, pp. 22–29, 2013.

[123] T. Miyazaki, Y. Takeda, S. Akane, T. Itou, A. Hoshiko, and K. En, "Role of boric acid for a poly (vinyl alcohol) film as a cross-linking agent: melting behaviors of the films with boric acid," *Polymer*, vol. 51, no. 23, pp. 5539–5549, 2010.

[124] L. L. Xia, C. L. Li, and Y. Wang, "In-situ crosslinked PVA/ organosilica hybrid membranes for pervaporation separations," *Journal of Membrane Science*, vol. 498, pp. 263–275, 2016.

[125] Q. G. Zhang, Q. L. Liu, Z. Y. Jiang, and Y. Chen, "Anti-trade-off in dehydration of ethanol by novel PVA/APTEOS hybrid membranes," *Journal of Membrane Science*, vol. 287, no. 2, pp. 237–245, 2007.

[126] K. C. S. Figueiredo, T. L. M. Alves, and C. P. Borges, "Poly(vinyl alcohol) films crosslinked by glutaraldehyde under mild conditions," *Journal of Applied Polymer Science*, vol. 111, no. 6, pp. 3074–3080, 2009.

[127] A. K. Sonker, "Crosslinking of polyvinyl alcohol (PVA) and effect of crosslinker shape (aliphatic and aromatic) thereof," *Journal of Polymers and the Environment*, vol. 26, 2017.