Journal of Materials and Environmental Science
ISSN : 2028-2508
e-ISSN : 2737-890X
CODEN : JMESCN

J. Mater. Environ. Sci., 2023, Volume 14, Issue 10, Page 1236-1252

http://www.jmaterenvironsci.com

A Comprehensive Review on Properties of Polyvinyl Alcohol (PVA) Crosslinked with Carboxylic Acid

Pragya Sharma [1] *, Pawan Kumar Agrawal [1], V. K. Singh [1], Sakshi Chauhan [1], Jitendra Bhaskar [2]

[1]*Department of Mechanical Engineering, G. B. Pant University of Agriculture & Technology, Pantnagar-263145, India*
[2]*Mechanical Engineering Department, Harcourt Butler Technical University, Kanpur-208002, India*
**Corresponding author, Email address: pragyas2007@gmail.com*

Received *04 Sept 2023,*
Revised *06 Oct 2023,*
Accepted *07 Oct 2023*

Keywords:
- ✓ *Polyvinyl Alcohol (PVA);*
- ✓ *Polymer matrix composites;*
- ✓ *Physical and Mechanical properties;*
- ✓ *Carboxylic acid crosslinking;*

Citation*: Pragya Sharma, Pawan Kumar Agrawal, V. K. Singh, Sakshi Chauhan, Jitendra Bhaskar (2023) A Comprehensive Review on Properties of Polyvinyl Alcohol (PVA) Crosslinked with Carboxylic Acid, J. Mater. Environ. Sci., 14(10), 1236-1252*

Abstract: Due to its biocompatible, non-toxic, and biodegradable characteristics, polyvinyl alcohol (PVA) is a versatile and highly sought-after thermoplastic polymer. Due to its remarkable mechanical and thermal characteristics, it can be used in a variety of applications. Although hydrophilicity is still a serious drawback, researchers have tried to lessen it by acid cross-linking PVA-based composites. The most alluring and popular technique for altering PVA's characteristics to make it a more desirable substance is cross-linking. For PVA cross-linking, several carboxylic acids have already been employed in processes including fuel cells, reverse osmosis (RO), wound dressing, and pervaporation. The various studies on carboxylic acid cross-linked PVA that are currently available are compiled in this review and used to create correlations between the structure and properties of cross-linked PVA. Additionally, a summary of the benefits and drawbacks of several carboxylic acids as PVA cross-linkers for various application domains is provided.

1. Introduction

Polyvinyl alcohol (PVA) is a synthetic, linear, semicrystalline polymer having a functional group of hydroxyl and a carbon chain acting as the backbone. By hydrolyzing polyvinyl acetate in ethanol with potassium hydroxide, Hermann and Haehnel produced polyvinyl alcohol (PVA) in 1924. It is manufactured for use in commerce using a continuous process and polyvinyl acetate. When either anhydrous sodium methylate or aqueous sodium hydroxide are present, the acetate groups are hydrolyzed by ester exchange with methanol. The degree of polymerization and hydrolysis determines physical properties and specific functional applications. There are two types of polyvinyl alcohol: partially hydrolyzed and fully hydrolyzed. The meals contain PVA that has been partially hydrolyzed. It is created by hydrolyzing polyvinyl acetate, and the amount of hydrolysis—whether complete or partial—affects the substance's physical characteristics. As a result, two varieties of PVA—fully and partially hydrolyzed—are available for purchase on the market. Since the length of polymeric chains varies, it is also accessible in a range of molecular weights (Saxena *et al.*, 2004), (Goodship *et al.*, 2009), (Agrawal *et al.*, 2023).

In the early 20th century, PVA, a synthetic polymer, was used on a global scale. In the industrial, commercial, medical, and culinary industries, it has been used to make a variety of end products, including lacquers, resins, surgical threads, and food packaging materials that frequently come into contact with food. PVA is a typical thermoplastic polymer that is harmless, nontoxic, and safe for living tissues. This polymer is extensively researched as a result of its use in cross-linked products and nanofillers (Qiu *et al.*, 2012; Qiu *et al.*, 2013). The hydroxyl groups on the carbon atoms in PVA make it more biodegradable through hydrolysis, making it a biodegradable polymer. Additionally, it has a hydrophilic character and is water soluble (Cho *et al.*, 2012; Lou *et al.*, 2003; Chiellini *et al.*, 2003; Solaro *et al.*, 2000; Vijayalakshmi *et al.*, 2006). For several polymers, including PVA, the rates and environmental factors that influence decomposition might vary. These factors include composting in the presence of oxygen, beneath soil layers, in aqueous media, and even in anaerobic environments (Corti *et al.*, 2012; Chiellini *et al.*, 1999; Jayasekara *et al.*, 2003). The chemical structure of polyvinyl alcohol is shown in Figure 1.

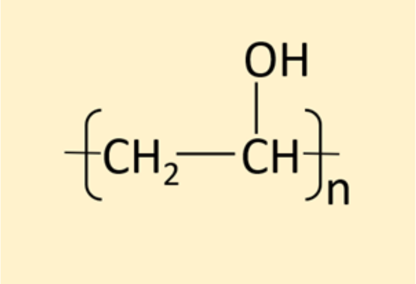


Figure 1. Chemical structure of polyvinyl alcohol (PVA)

The inclusion of hydroxyl groups increases the water adsorption capacity of PVA and makes it water soluble, which reduces its mechanical and electrical properties. Its use is therefore constrained by its thermal characteristics. By partially cross-linking the polymer chains, water adsorption or water solubility can be managed (Sapalidis, 2012; Rohatgi *et al.*, 2015). The creation of chemical links between several polymer chains is known as cross-linking. It is a tried-and-true, uncomplicated approach for getting new materials with better attributes. Cross-linking limits the mobility of polymeric chains at the microscopic level, which may have an impact on the crystal structure, crystal size distribution, and crystallinity level (Heydari *et al.*, 2013). In general, cross-linking increases the amorphous region while decreasing the degree of crystallinity.

In PVA, hydroxyl groups are used for cross-linking. As a result, PVA's partial cross-linking has a less dense number of hydroxyl groups accessible for forming hydrogen bonds with water and a lower capacity for absorbing water. Cross-linking also reduces chain movability, which in turn limits the swelling of polymers and regulates the free volume of water molecules within the polymeric matrix (Sonker *et al.*, 2018). Cross-linking strengthens the mechanical and thermal resilience of PVA by forming chemical links between various components (Maitra *et al.*, 2014). PVA is capable of being cross-linked employing either a physical method or a chemical process, which are the two different methods available. While gamma irradiation and freeze-thawing are examples of physical cross-linking, chemical cross-linking uses reactive substances that can interact with the hydroxyl groups in the structure of PVA to join the two distinct polymeric chains (Heydari *et al.*, 2013; Sanchez *et al.*, 2019; Marín *et al.*, 2014). PVA cross-linking through physical means is less common due to its high cost, difficulty in regulating the extent of cross-linking, and potential damage to polymer chains (Marín *et al.*, 2014). Contrarily, chemically altering the hydroxyl groups in PVA by the use of cross-linking agents is easier, more affordable, and controllable.

There have been reports of both organic and inorganic substances acting as PVA cross-linkers, including dialdehydes, acid anhydrides, diisocynates, transglutaminase, polyurethane, genipin, boric acid, epichlorohydrin, mono/di/polycarboxylic acids, alkoxysilane, dimethyl carbonate, epoxy compounds, polyphenol, carboxymethyl-chitosan, and acrylic acid. But some of them have disadvantages, such as being cytotoxic, having disagreeable odors, making PVA nonbiodegradable, or having a negative impact on the various properties of PVA (Reddy *et al.*, 2015). Particularly, these cross-linkers restrict the application of PVA in the food packaging sector.

New, environmentally sustainable cross-linkers have been discovered as the scientific community shifts its focus towards the advancement of green technologies (Bensouda *et al.*, 2019), (Majidi *et al.*, 2010). The evaluation of the carboxylic acid cross-linked PVA involved examining its various physicochemical characteristics. One of these cross-linking agents for PVA, carboxylic acids, has attracted a lot of attention from the scientific community over the past 10 years. Carboxylic acids are commonly referred to as "green cross-linking agents" since they are readily available, odorless, environment-friendly, affordable, nontoxic, biodegradable, and non-accumulative in nature. They also don't need any special expertise to be used as cross-linking agents (Pangon *et al.*, 2016). Figure 2 depicts the cross-linking process between PVA and carboxylic acid that results in the creation of cross-linked PVA. As they contain two or more reactive sites that aid in the production of a strong, stable, and a high level of cross-linked network, certain carboxylic acids, such as dicarboxylic and polycarboxylic acids, and their derivatives, are discovered to be employed as effective cross-linkers (Xu *et al.*, 2018). These acids possess two or more reactive carboxylic groups with functionalities that react with the hydroxyl groups in PVA in an esterification reaction to produce various sorts of covalent bonds that are both inter- and intramolecular.

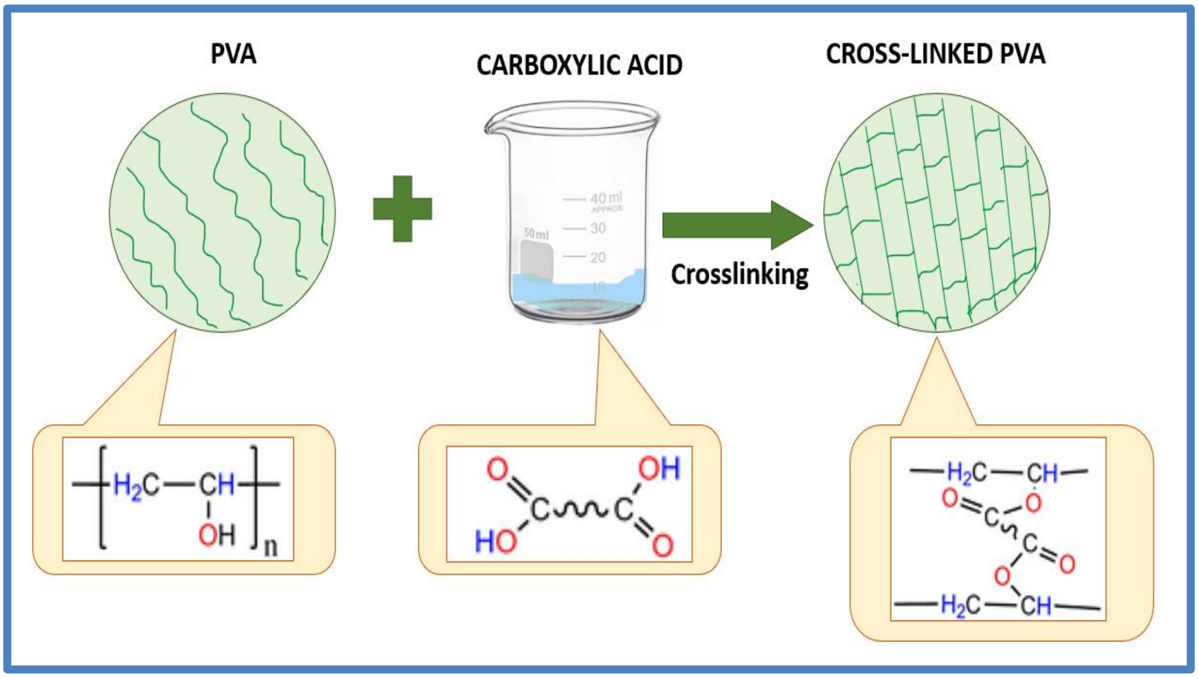


Figure 2. Cross-linking process between PVA and carboxylic acid

The degree of cross-linking can be assessed using Fourier transform infrared (FTIR)/attenuated entire reflection-FTIR analysis, which also confirms the cross-linking reaction, while the hydrophilic/hydrophobic properties can be assessed using contact angle measurement. By using atomic force microscopy and scanning electron microscopy, certain researchers have also examined the morphology of the membrane (Sonker *et al.*, 2018), (Dlamini *et al.*, 2014), (Do Nascimento *et al.*, 2018). Numerous studies used X-ray diffraction (XRD) to examine the crystalline and polymorphic characteristics of cross-linked polymer material as well as its mechanical properties through tensile strength testing (Kudoh *et al.*, 2013).

2. Usage of a Variety of Carboxylic Acids as Cross-Linking Agent

In various applications, carboxylic acids can be utilized as cross-linking agents. By creating chemical links between polymer chains, a process known as cross-linking, a three-dimensional network structure is produced. This network improves the material's mechanical characteristics, such as strength and durability. A carboxyl group (-COOH), which is made up of a carbonyl group (C=O) and a hydroxyl group (OH) connected to the same carbon atom, is present in carboxylic acids. By reacting with other functional groups present in the polymer chains, such as amino groups (-NH2) or hydroxyl groups (-OH), the carboxyl group can take part in cross-linking activities. Table 1 lists various carboxylic acids that have been used as a cross-linking agent for PVA. PVA has frequently been cross-linked by various carboxylic acids, including mono-, di-, tri-, and polycarboxylic acids, as well as by these acids' derivatives, such as acid anhydrides and acid chlorides.

Formic acid (Wang *et al.*, 2017) has been used as monocarboxylic acid whereas a large number of dicarboxylic acids such as oxalic acid, (Gohil *et al.*, 2009) malonic acid, (Qiu *et al.*, 2013) succinic acid (Kudoh *et al.*, 2013), glutaric acid (Hrabalikova *et al.*, 2016), adipic acid (Sonker *et al.*, 2016), malic acid (Işıklan *et al.*, 2005), fumaric acid (Heydari *et al.*, 2013), Malic Acid (Riyajan *et al.*, 2009), tartaric acid (Chaudhari *et al.*, 2015), suberic acid, terephthalic acid, (Sonker *et al.*, 2018), 4-sulfopthalic acid (Xue *et al.*, 2015), sulfosuccinic acid (SSA), (Alaknanda, 2017) and furan dicarboxylic acid (Salgado *et al.*, 2020) have been used as cross-linkers. Although some studies have also utilized aconitic acid (Dlamini *et al.*, 2014) in this series, CA (Natraj *et al.*, 2020; Zhu *et al.*, 2018) is the butane- 1,2,3,4-tetracarboxylic acid (Cay *et al.*, 2017; Zhao *et al.*, 2007) is one of the polycarboxylic acids that have been studied. The use of maleic anhydride, ethylenediaminetetraacetic dianhydride, 3,3,4,4-benzophenone tetracarboxylic dianhydride (BTDA), 4,4-oxydiphthalic anhydride (ODPA), and pyromellitic carboxylic acid dianhydride (PMDA) as cross-linking agents are among the acid anhydrides.

Table 1. Various carboxylic acids used as a cross-linking agent for PVA

Name of Carboxylic Acid	Structure	Functional Group	Application
1,2,3,4-butanetetracarboxylicacid	Tetracarboxylic acid (aliphatic)	4 COOH	Waste water treatment Tissue engineering Food packaging Wound dressing (Cay *et al.*, 2017; Akduman *et al.*, 2021; Song *et al.*, 2014; Pangon *et al.*, 2016)
3,3,4,4-benzophenone tetracarboxylic dianhydride	Acid anhydride (aromatic)	Anhydride	Pervaporation (Xu *et al.*, 2018)
4-sulfophthalic acid	Dicarboxylic acid (aromatic)	2 COOH 1 SO3H	Fuel cell Pervaporation (Cadinelli *et al.*, 2018; Xue *et al.*, 2015)
Aconitic acid	Tricarboxylic acid (unsaturated)	3 COOH	Development of polysulfone membranes

			(Dlamini *et al.*, 2014)
Adipic acid	Dicarboxylic acid (aliphatic)	2 COOH	PVA supported catalytic membranes Solid polymer electrode (Casimiro *et al.*, 2014)
Citric acid	Tricarboxylic acid (aliphatic)	3 COOH 1 OH	Fuel cell Tissue engineering Food packaging Wound dressing Drug delivery Desalination Hemodialysis (Birck *et al.*, 2014 ; Ghorpade *et al.*, 2019 ; Nulik *et al.*, 2017 ; Velutheril *et al.*, 2019 ; Lusiana *et al.*, 2013 ; Gulenorr *et al.*, 2016)
Ethylenediaminetetraacetic dianhydride	Acid anhydride	Anhydride	Pervaporation (Xu *et al.*, 2018)
Formic acid	Monocarboxylic acid	1 COOH	Separation process (Wang *et al.*, 2017)
Fumaric acid	Dicarboxylic acid (unsaturated)	2 COOH	Drug delivery Pervaporation (Tran *et al.*, 2016), (Quan *et al.*, 2020)
Furandicarboxylic acid	Dicarboxylic acid (aromatic)	2 COOH	Separation process (Salgado et al., 2020)
Glutaric acid	Dicarboxylic acid (aliphatic)	2 COOH	Desalination Food packaging (Hrabalikova *et al.*, 2016; Kumar *et al.*, 2020)
Maleic acid	Dicarboxylic acid (unsaturated)	2 COOH	Wound dressing Reverse osmosis Metal uptake in aqueous systems (Saraf *et al.*, 2014 ; Avila-Salas *et al.*, 2019 ; Truong *et al.*, 2017)
Maleic anhydride	Acid anhydride	Anhydride	Separation process Drug delivery Reverse osmosis (Salgado *et al.*, 2020 ; Maji *et al.*, 2013 ; Samnani *et al.*, 2018)
Malic acid	Dicarboxylic acid (aliphatic with additional hydroxyl group)	2 COOH 1 OH	Drug delivery Pervaporation Food packaging Reverse osmosis Waste water treatment (Tran et al., 2016 ; Hieu et al., 2016 ; Valdes et al., 2018)
Malonic acid	Dicarboxylic acid (aliphatic)	2 COOH	Iodine Release systems, Lithium-ion battery membrane Biomaterials

			(Khodaverdi *et al*., 2021; Liu *et al*., 2020)
Oxalic acid	Dicarboxylic acid (aliphatic)	2 COOH	Food packaging, Solid Polymer Electrolyte (Fattoum *et al*., 2015; Suganthi *et al*., 2018)
Pyromellitic carboxylic acid	dianhydride Acid anhydride (aromatic)	Anhydride	Pervaporation (Xu *et al*., 2018)
Suberic acid	Dicarboxylic acid (aliphatic)	2 COOH	Solid Polymer Electrolyte Sensors (Sonker *et al*., 2018)
Succinic acid	Dicarboxylic acid (aliphatic)	2 COOH	Wound Dressing Food packaging Drug delivery Fuel cell (Suganthi *et al*., 2018), (Avila-Salas *et al*., 2019), (Quan *et al*., 2020), (Kumar *et al*., 2020), (Alaknanda et al., 2016)
Sulfosuccinic acid	Dicarboxylic acid (aliphatic with additional sulfo group)	2 COOH 1 SO_3H	Pervaporation Solid Polymer Electrolyte Waste Water Treatment (Gonzalez *et al*., 2018), (Xue *et al*., 2020), (Yoon *et al*., 2019)
Tartaric acid	Dicarboxylic acid (aliphatic with additional two hydroxyl groups)	2 COOH 2 OH	Food packaging Pervaporation Tissue Engineering (Suganthi *et al*., 2020), (Sonker *et al*., 2019)
Terephthalic acid	Dicarboxylic acid (aromatic)	2 COOH	Development of polysulfone membranes (Dlamini *et al*., 2014)

3. Impact of various carboxylic acids on the characteristics of cross-linked PVA

The carboxylic acid cross-linking procedure affects the physicochemical properties of PVA, including its chemical composition, hydrophilicity, and degree of swelling. When used as cross-linking agents, various carboxylic acids can have a variety of effects on the characteristics of the cross-linked polyvinyl alcohol (PVA) material. The effects of carboxylic acid molecular structure on the properties of cross-linked PVA are summarized in Figure 3.

The presence of other functional groups, the type of hydrocarbon chain attached to the carboxylic group in the acid (aliphatic, unsaturated, or aromatic), the density of the carboxylic group in the acid (mono, di, tri, or tetra), and the cross-linking processing parameters, such as the amount of cross-linker, the cross-linking time, and the operating temperature of the cross-linking reaction, all affect how much the properties of PVA are modified (Suganthi *et al*., 2018).

One essential quality of hydrogels is their hydrophilicity. A lot of water can be absorbed by nanopores made of PVA-based hydrogels that have been cross-linked with polycarboxylic acids without dissolving in it (Avila-Salas *et al*., 2018). The type and concentration of the crosslinker have a significant impact on the pore size of the cross-linked PVA. Therefore, the degree of crosslinking enables the modification of hydrogel pore size.

Numerous investigations have demonstrated that a high cross-linking agent content combined with PVA resulted in a stiffer, more compact structure with less structural porosity (Hoare *et al.*, 2008). It was also shown that the hydrophilic properties of the cross-linked PVA were influenced by the chemical composition of the cross-linking agents. Because succinic acid and malic acid both contain a comparable number of carbon atoms, but succinic acid has one more hydroxyl group than malic acid, it has been shown that the amount of hydroxyl groups present in a cross-linker influences the hydrophilic qualities of cross-linked PVA material. Crosslinked PVA membranes' hydrophilicity is further constrained by the presence of two bonds in the carboxylic acid due to the strong interlocking of polymeric chains and the development of a stiffer, tightly packed structure (Tran *et al.*, 2016).

In terms of geometrical isomerism, fumaric acid and MA are both carboxylic acids; fumaric acid, however, exhibits trans isomerism as opposed to MA's cis structure, and its steric hindrance impact is lower than MA's. A carbon double bond can be seen on the molecules of both of these carboxylic acids (Tran *et al.*, 2016). As a result, transposition of the reactive group caused fumaric acid PVA to be less hydrophilic than MA PVA and to cross-link with PVA more strongly than cis. The high sulfonic group content of the cross-linkers promotes more water molecule transit while also increasing PVA's hydrophilicity. Furthermore, it was shown that the sulfonic group-containing cross-linking agent 4-sulfophthalic acid increased the density of hydrogen bonds between water molecules.

Carbon Chain Length	• Greater space between the PVA chains with more carbon atoms, hydrophilicity rises as the number of carbon atoms increases.
Number of Carboxylic group	• Swelling diminishes when the number of carboxylic acids grows due to the improved inclination for cross-linking.
Saturation and Unsaturation	• The tight interlocking of polymeric chains caused by double bonds limits hydrophilicity.
Aliphatic/Aromatic	• Since aliphatic chains easily infiltrate polymeric chain networks, they have greater cross-linking and hence exhibit less swelling.
Position of Carboxylic group in aliphatic chain (cis/trans)	• The polymer chain is substantially more densely packed in the trans form, which further improves selectivity, cross-linking, and hydrophilicity.
Position of carboxylic group in aromatic chain (ortho/meta/para)	• Less steric hindrance allows for better cross-linking, which results in less hydrophilicity being imparted. Therefore, para position is more appropriate for crosslinking.
Presence of additional groups (-OH & -SO3H group)	• Sulfonic and hydroxyl groups increase the density of hydrogen bonds with water molecules, which consequently contributes to an increase in hydrophilicity.

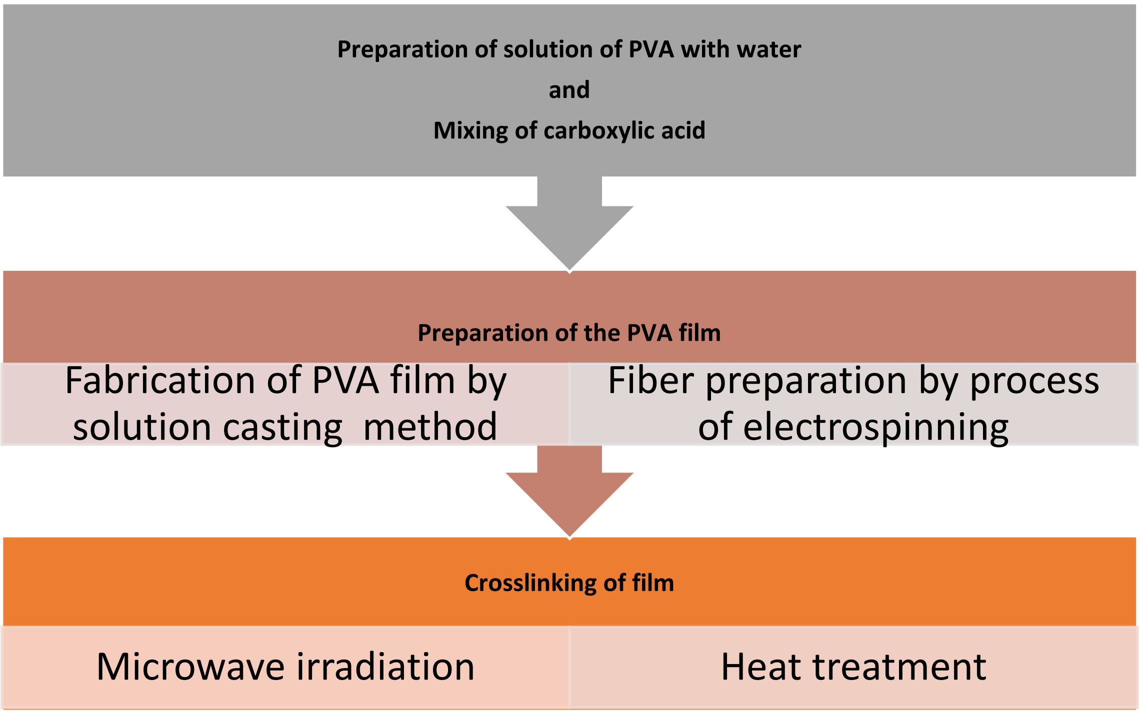
Figure 3. Effect of molecular structure of carboxylic acids on characteristics of cross-linked PVA.

This improves the water flux in membrane-based separation applications (Xue *et al.*, 2015), (Xue *et al.*, 2020). Aliphatic carboxylic acids are also more effective as PVA cross-linkers than aromatic carboxylic acids because they can enter the polymeric chain network more easily. Where the carboxylic group is positioned affects how effective aromatic carboxylic acids are. It was discovered that ortho positioning of the carboxylic acid-containing groups had higher steric hindrance than meta or para positioning. Because terephthalic acid has carboxylic groups in the para position rather than the ortho position, it is believed to be more suitable for PVA cross-linking than phthalic acid (Dlamini *et al.*, 2014).

4. Carboxylic Acid Crosslinked PVA Preparation Method

According to published research, three stages are used to create carboxylic acid cross-linked PVA films (Figure 4). The first one is creating a solution with water by mixing PVA and carboxylic acid. The second step is fiber preparation or casting the film. In the third step, the polymer cross-linker is heated further either direct heating or microwave irradiation (Dlamini *et al.*, 2014), (Nguyen *et al.*, 2019).

By electrospinning, cross-linked PVA fibers can be made. The polymeric solution is exposed to a strong electrical field throughout this operation. Electrical potential is used to drive the polymeric solution towards the oppositely charged plate. During this procedure, the solution created a nanometer-sized fiber structure (Fathi *et al.*, 2014). This procedure produces nanofiber nets or sheets that are utilized as membranes for tissue engineering, wound treatment, and separation procedures (Xue *et al.*, 2019). In many investigations, the carboxylic acid cross-linked PVA was produced by electrospinning (Natraj *et al.*, 2020), (Cay *et al.*, 2017).



Preparation of solution of PVA with water
and
Mixing of carboxylic acid

Preparation of the PVA film

Fabrication of PVA film by solution casting method

Fiber preparation by process of electrospinning

Crosslinking of film

Microwave irradiation

Heat treatment

Figure 4. Fabrication process of carboxylic acid cross-linked PVA films.

A common method for creating polymeric films, sheets, and membranes is solution casting. Cross-linked polymers are highly suited to this procedure. Employing a polished blade (doctor blade), polymeric solution is cast onto the film using this technique on a flat surface. The solvent is then eliminated via a phase inversion or evaporation process (Krstic *et al.*, 2017). This procedure is particularly reported for PVA films that have been cross-linked with carboxylic acids for use in food packaging (Suganthi *et al.*, 2018), (Suganthi *et al.*, 2020). The cast film or fibers must undergo additional processing in order to complete the esterification reaction and produce the necessary level of cross-linking. This can be done by either direct thermal treatment or microwave irradiation.

A straightforward technique is the heat treatment method, which involves thermally treating a produced PVA film that has been cross-linked with carboxylic acid as the cross-linker at a high temperature in an air oven for a predetermined amount of time (Tran *et al.*, 2016), (Kumeta *et al.*, 2004). Such heat treatment changes the crystalline structure of cross-linked PVA film or membrane by facilitating the esterification reaction between PVA and carboxylic acid to generate cross-link network (Wang *et al.*, 2019), (Zhang *et al.*, 2019).

Another method besides the traditional heating method that has been employed as a source of heat for PVA cross-linking is the microwave irradiation method. It offers a higher yield than thermal treatment and shortens the cross-linking reaction's time (Sonker *et al.*, 2018), (Nguyen *et al.*, 2019). When PVA crosslinked by dicarboxylic acid was compared to microwave irradiation and traditional heat treatment, it demonstrated that the former process produces better characteristics (Sonker *et al.*, 2018). In a related study, the direct heating approach and films made of cellulose-PVA composite that had been cross-linked with tartaric acid were compared (Sonker *et al.*, 2019). In this study, it was discovered that microwave-prepared composites and conventionally heated composites exhibit identical qualities, although microwave preparation only requires 14 minutes as opposed to 2 hours for direct heating.

5. Carboxylic Acid Crosslinked PVA Applications

As a hydrophilic and mechanically robust polymer, carboxylic acid cross-linked PVA has been found to have applications in biomedicine. It has also been used as food packaging material to shield meals from spoiling and damage. It has also been acknowledged as a flexible material for the synthesis of membranes for separation applications due to its high-water flux, antifouling properties, and behaviour that is both thermally and chemically robust. Several of the main applications for carboxylic acid cross-linked PVA are shown in Figure 5.

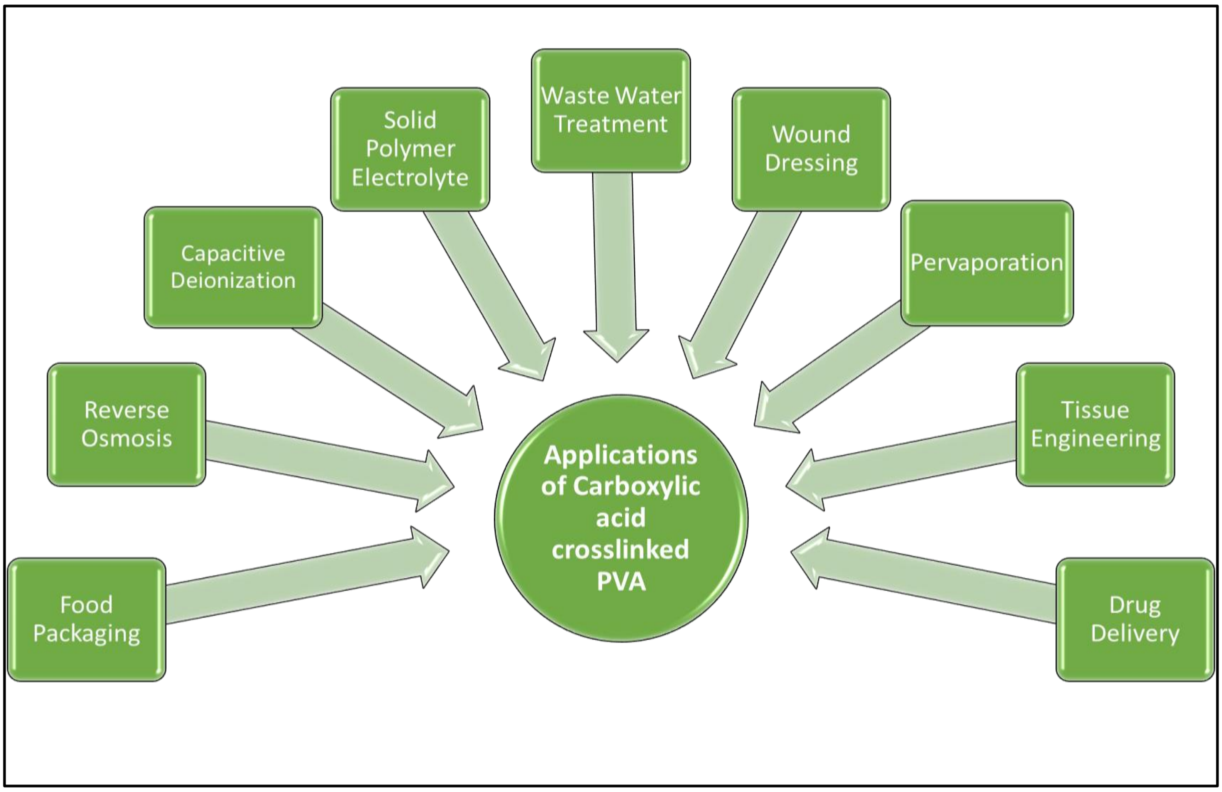


Figure 5. Applications in which carboxylic acid cross-linked PVA is used.

Cross-linked PVA has been used in a variety of applications, including drug delivery, tissue engineering, wound dressing, food packaging, antibacterial membranes against polluted air, reverse osmosis (RO) membranes for desalination of water, pervaporation process, filtration/separation of metal ions, and solid electrolytes made of polymers (Alaknanda, 2017; Fattoum *et al.*, 2015). Through a procedure known as tissue engineering, artificial/natural tissues are produced in labs. Biocompatible polymers that promote the growth and proliferation of seeded cells are required for this. PVA is a suitable and biocompatible candidate for tissue engineering applications. It becomes more beneficial when it is crosslinked with the green crosslinkers, carboxylic acids. Numerous studies on PVA cross-linked with carboxylic acid for medical applications have been reported.

For use in medicine, CA cross-linked PVA nanofibers were created (Salgado *et al.*, 2020). The cross-linked fibers were examined for moisture resistance, elongation, thermal properties, and biocompatibility after cross-linking was carried out at 1500 C and validated by FTIR. Cross-linking is said to have improved the fibers' thermal stability and elasticity as well as their water resistance. Cross-linked PVA nanofibrous mats were found to be beneficial for promoting the growth and proliferating fibroblast cells, according to experiments conducted in cell culture. A different study (Pangon *et al.*, 2016) generated PVA/chitosan electrospun nanofibers utilizing the electrospinning technique and cross-linked them with three distinct multicarboxylic acids, namely succinic acid (diacid), CA (triacid), and 1,2,3,4-BTCA (tetraacid). The nanofibrous membrane's swelling characteristics could be adjusted by cross-linking with various carboxylic acids.

Transparent, flexible films made of PVA that have been cross-linked using carboxylic acids can be handled with ease while treating wounds. These films allow for step-by-step assessment of the healing process and stronger mechanical protection. The manufacture of the hydrophilic hydrogel-based wound treatment using PVA cross-linked with carboxylic acid has been the subject of numerous studies. (Zhu *et al.*, 2018), (Avila-Salas *et al.*, 2019), (Ponco *et al.*, 2020), (Cay *et al.*, 2013). In a theoretical study, cross-linked PVA hydrogels' drug release characteristics for 20 distinct carboxylic acids were assessed using a molecular dynamics technique. Succinic, aspartic, maleic, and malic acids cross-linked PVA was discovered to be the best hydrogel for wound healing applications during in vivo testing (Avila-Salas *et al.*, 2019). The results of an experimental study showed that the films were effective in quickening the healing of fake wounds in rats. They also demonstrated outstanding biocompatibility and were recommended as extremely promising dressing materials for skin wound healing (Hieu *et al.*, 2016).

Similar to this study, (Ponco *et al.*, 2020) CA cross-linked PVA with CMC blending was used to create the hydrogels. In this study, CuNPs were additionally added to hydrogel to create an antibacterial substance. At 70˚C for roughly 16 hours, esterification was used to create chemical cross-links. When used against Staphylococcus aureus and Escherichia coli, the produced hydrogel nanocomposites were successful. Additionally, (Cay *et al.*, 2017) the evaluation of 1,2,3,4-BTCA and CA-crosslinked electrospun PVA nanofibers for use as a wound dressing. For 30 minutes, cross-linking was carried out at 180˚C. The findings showed that films held up well in water. In comparison to BTCA cross-linked films, the degree of swelling was observed to be greater for CA cross-linked films. However, it was discovered that both types of films' toxicity and cell proliferation performance attributes were excellent, and they could be used as wound dressings. Similar to this, PVA nanofibers produced using the electrospinning technique were cross-linked using 1,2,3,4-BTCA as the cross-linker (Cay *et al.*, 2013). The findings suggested that electrospun nanofibrous PVA-BTCA is a useful material for wound dressings since it is nontoxic and stable in water.

Carboxylic acid crosslinking of PVA produces polymers with potent water-soluble chemical adsorption and penetration properties. Therefore, cross-linked PVA can be used to control how water-soluble medicine is dispersed. As a result, it deserves research and consideration for application as a mechanism of drug administration through cross-linking with different carboxylic acids. When creating a PVA-based formulation for medicine delivery, twenty dicarboxylic acids were utilised as cross-linkers. (Wilson, 2011). Prednisone drug release was examined in a controlled setting throughout this investigation. PVA with succinic acid crosslinks had the best drug release characteristics. Additionally, the developed materials demonstrated superb mechanical qualities and remarkable biocompatibility with mouse connective tissue fibroblasts. They can be used to release medications to treat dermatological conditions.

In a related study, (Ghorpade *et al.*, 2019) solution-cast PVA and CMC hydrogel films that were cross-linked with CA as a cross-linking agent were created. The films were examined for the release of the water-soluble medication gentamicin sulphate. The films that were created were hemocompatible. The hydrogel films made of CMC-PVA were discovered to be suitable biomaterials for delivering the water-soluble medication. For the delivery of pH-responsive and antibacterial drugs, PVA/CA/AgNP hydrogels were created (Sabzi *et al.*, 2020). The results of this work demonstrated that the unbound carboxylic acid groups on CA are not only responsible for cross-linking but also for the pH sensitivity and antibacterial activity of PVA hydrogels.

PVA is a potentially useful substance for use in fuel cells since it is inexpensive, environmentally acceptable, and has adaptable qualities. However, because PVA lacks sufficient negatively charged ions, it is a poor proton conductor. This limitation can be solved by incorporating the charge-conducting polymer and then cross-linking it with carboxylic acid or its derivatives. Using the solution casting process, proton-conducting films based on PVA were created (Cadinelli *et al.*, 2018); the cross-linkers utilized were CA and 4-sulfophthalic acid. The synthesised films were characterised using TGA, swelling intensity, relative refractive index, real part of dielectric constant, spectroscopic ellipsometry, and electrochemical impedance spectroscopy (EIS). After conductivity measurements of the synthesised cationic films were compared with Nafion, a widely available membrane by EIS, and found to be identical, cross-linked PVA cationic membranes were identified to be potential materials to be used as proton exchange membranes. An ion-conducting polymeric electrolyte was made by crosslinking PVA and succinic acid using a method similar to solution casting (Alaknanda *et al.*, 2016). The DC conductivity of PVA increased with increasing succinic acid concentration, according to the results. But when the concentration increased, the conductivity began to decrease.

In a related study, solution casting was used to create a polymeric membrane based on PVA and SSA as a cross-linker and then it was compared to commercial Nafion membrane (Alaknanda, 2017). The PVA/SSA ionomer is just as efficient at the anode catalytic layer as Nafion, according to this study. Although a cell based on a cross-linked membrane was only found to have a 35% greater power density than a cell based on a Nafion membrane, it was also found to be less expensive, making it a viable option for large-scale proton exchange membrane fuel cell production.

Pervaporation is a safe, cost-effective, and energy-efficient method for separating different components from a liquid mixture in situations where distillation procedures fail. Using a hydrophilic membrane constructed of cross-linked PVA, it is usual practice to remove pollutants from water from organic mixes, such as alcohol dehydration. Numerous scientists from around the world have expressed interest in cross-linked PVA in this area. An asymmetric SSA cross-linked PVA membrane was made by casting the PVA/SSA combination on a porous polyacrylonitrile (PAN) ultrafiltration membrane.

(Sabzi *et al.*, 2020). Cross-linked membranes were discovered to have excellent water permeability and relatively less swelling than non-cross-linked membranes.

In a related study, (Tran *et al.*, 2016) solution casting was used to create a PVA-based composite membrane covered on a PAN permeable support membrane. Malic acid, MA, and fumaric acid were the three different carboxylic acids used as cross-linkers. The swelling level, permeation flux, and separation factor of the generated membranes were all found to follow a pattern that moved from malic acid-PVA through fumaric acid-PVA to plain PVA. Dicarboxylic acids were found to cross-link PVA membrane at high temperatures, resulting in a larger separation factor but a reduced flow. Similar solution casting techniques were employed to produce tartaric acid cross-linked PVA pervaporative membranes, which were then tested for acetic acid dehydration separation. (Chaudhari *et al.*, 2015). FTIR, swelling analyses, DSC, and measurements of contact angle were used to confirm cross-linking. According to the findings', produced membranes are more capable of separating substances from liquids and have a higher water permeability.

By utilising MA as a crosslinker, a hybrid polymer-inorganic PVA/silica particles composite membrane was created (Xie *et al.*, 2011). Cross-linkers were discovered to reduce the swell and crystalline structure of the membrane. On the other hand, silica nanoparticles added to the PVA matrix improved the membrane's water permeability by increasing the free volume.

Ions from the liquid mixture are kept inside conductors with opposing charges during the CDI desalination process, and they are then released upon the application of a reverse potential. The CDI process is regarded as an energy-efficient process because it operates at a very low voltage and no electrolytic reactions occur. Gaining more wetted surface area is essential for improving CID effectiveness. Cross-linked PVA can be a good contender for improving the water-holding capacity of polymer-bonded carbon electrodes because of its hydrophilic characteristics

Conclusion

This review demonstrates that, cross-linking of PVA with carboxylic acids involves an esterification reaction between the carboxyl groups of the acids and the hydroxyl groups of PVA. However, an unreacted cross-linked network is produced when PVA is cross-linked using several carboxylic acids. The selectivity of the polymer matrix is provided by these groups. In fact, the three-dimensional PVA cross-linked network is more stable and has numerous ester connections when multi carboxylic acids are used as cross-linkers. By adding new reactive groups, crosslinking makes the PVA include more active sites. Because it has hydrophilic groups that allow the network to interact with water molecules and hydrophobic groups that increase the repellency of solid particles and other molecules, cross-linked PVA is an excellent material for creating membranes for separation operations. On the other hand, polycarboxylic acids, which are safe chemicals and eco-friendly cross-linkers, are widely used in circumstances where toxicity is a concern, such as in food packaging materials. Cross-linker concentration, cross-linking duration, and curing temperature are some of the factors that affect how PVA carboxylic acids cross-linked membranes are modified. As an outcome of the cross-linking reaction with carboxylic acids, PVA experiences a number of changes in its properties, including a decrease in the crystallinity of its structure, increased mechanical and thermal stability, a decrease in hydrophilicity, an increase in water stability, antibacterial activity, and proton transport. PVA-based membranes are now highly adaptable and can be used in a wide range of processes, including pervaporation, supporting membrane in RO, drug delivery system, antimicrobial food packaging, fuel cells, desalination, air filter, biodiesel synthesis, ion exchange, and metal separation.

Disclosure statement: *Conflict of Interest:* The authors declare that there are no conflicts of interest. *Compliance with Ethical Standards:* This article does not contain any studies involving human or animal subjects.

References

Agrawal, P. K., Sharma, P., Singh, V. K., & Chauhan, S. (2023). A Comprehensive Review on the Engineering of Biocompatible Polyvinyl Alcohol Composites with Enhanced Properties Using Carbonaceous Fillers. *J. Mater. Environ. Sci.,* 14 (5), 560, 581.

Akduman, Ç., Morsümbül, S., & Kumbasar, E. P. A. (2021). The Removal of Reactive Red 141 From Wastewater: A Study of Dye Adsorption Capability of Water-Stable Electrospun Polyvinyl Alcohol Nanofibers. *Autex Research Journal,* 21(1), 20-31.

Alakanandana, S. (2017). electrical characterization of PVA doped malonic and succinic acid polymer electrolytes. *IJSTE,* 3, 30-35.

Alakanandanaa A, Subrahmanyam AR, Siva KJ (2016) Structural and electrical conductivity studies of pure PVA and PVA doped with succinic acid polymer electrolyte system. *Mater Today Proc* 3:3680–3688

Ávila-Salas, F., Marican, A., Pinochet, S., Carreño, G., Valdés, O., Venegas, B., ... & Durán-Lara, E. F. (2019). Film dressings based on hydrogels: Simultaneous and sustained-release of bioactive compounds with wound healing properties. *Pharmaceutics,* 11(9), 447.

Avila-Salas, F., Marican, A., Villaseñor, J., Arenas-Salinas, M., Argandoña, Y., Caballero, J., & Durán-Lara, E. F. (2018). In-Silico Design, Synthesis and Evaluation of a Nanostructured Hydrogel as a Dimethoate Removal Agent. *Nanomaterials,* 8(1), 23.

Bensouda, Z., El Assiri, E. H., Sfaira, M., Ebn Touhami, M., Farah, A., & Hammouti, B. (2019). Extraction, characterization and anticorrosion potential of an essential oil from orange zest as eco-friendly inhibitor for mild steel in acidic solution. *Journal of Bio-and Tribo-Corrosion*, 5, 1-20.

Birck, C., Degoutin, S., Tabary, N., Miri, V., & Bacquet, M. (2014). New crosslinked cast films based on poly (vinyl alcohol): Preparation and physico-chemical properties. *Express Polymer Letters*, 8(12).

Cadinelli, B. L. S., do Nascimento, F. C., Faria, T. A. A., Freire, L. M., da Silva, L., de Castro, J. A., & Brum, F. J. B. (2018). Synthesis and characterization by ellipsometry of cationic membranes for fuel cells. In Materials Science Forum (Vol. 930, pp. 625-630). Trans Tech Publications Ltd.

Casimiro, M. H., Silva, A. G., Alvarez, R., Ferreira, L. M., Ramos, A. M., & Vital, J. (2014). PVA supported catalytic membranes obtained by γ-irradiation for biodiesel production. *Radiation Physics and Chemistry,* 94, 171-175.

Cay, A., & Miraftab, M. (2013). Properties of electrospun poly (vinyl alcohol) hydrogel nanofibers crosslinked with 1, 2, 3, 4-butanetetracarboxylic acid. *Journal of applied polymer science,* 129(6), 3140-3149.

Çay, A., Akçakoca Kumbasar, E. P., Keskin, Z., Akduman, Ç., & Şendemir Ürkmez, A. (2017). Crosslinking of poly (vinyl alcohol) nanofibres with polycarboxylic acids: Biocompatibility with human skin keratinocyte cells. *Journal of Materials Science,* 52(20), 12098-12108.

Chaudhari, S., Kwon, Y., Moon, M., Shon, M., Park, Y., Song, H., ... & Nam, S. (2015). Water-selective Membrane from Crosslinking of Poly (vinyl alcohol) with Tartaric Acid and Its Pervaporation Separation Characteristics for a Water/Acetic Acid Mixture. *Bulletin of the Korean Chemical Society,* 36(10), 2534-2541.

Chiellini, E., Corti, A., & Solaro, R. (1999). Biodegradation of poly (vinyl alcohol) based blown films under different environmental conditions. *Polymer Degradation and Stability*, 64(2), 305-312.

Chiellini, E., Corti, A., D'Antone, S., & Solaro, R. (2003). Biodegradation of poly (vinyl alcohol) based materials. *Progress in Polymer science,* 28(6), 963-1014.

Cho, D., Netravali, A. N., & Joo, Y. L. (2012). Mechanical properties and biodegradability of electrospun soy protein Isolate/PVA hybrid nanofibers. *Polymer Degradation and Stability,* 97(5), 747-754.

Corti, A., Solaro, R., & Chiellini, E. (2002). Biodegradation of poly (vinyl alcohol) in selected mixed microbial culture and relevant culture filtrate. *Polymer Degradation and Stability,* 75(3), 447-458.

Dlamini, D. S., Wang, J., Mishra, A. K., Mamba, B. B., & Hoek, E. M. (2014). Effect of cross-linking agent chemistry and coating conditions on physical, chemical, and separation properties of PVA-Psf composite membranes. *Separation Science and Technology,* 49(1), 22-29.

Do Nascimento, F. C., de Aguiar, L. C. V., Costa, L. A. T., Fernandes, M. T., Marassi, R. J., Gomes, A. D. S., & de Castro, J. A. (2021). Formulation and characterization of crosslinked polyvinyl alcohol (PVA) membranes: effects of the crosslinking agents. *Polymer Bulletin*, 78(2), 917-929.

Fathi, M., Martín, Á., & McClements, D. J. (2014). Nanoencapsulation of food ingredients using carbohydrate based delivery systems. *Trends in Food Science & Technology,* 39(1), 18-39.

Fattoum, A., Arous, M., Pedicini, R., Carbone, A., & Charnay, C. (2015). Conductivity and dielectric relaxation in crosslinked PVA by oxalic and citric acids. *Polymer Science Series* A, 57, 321-329.

Ghorpade, V. S., Dias, R. J., Mali, K. K., & Mulla, S. I. (2019). Citric acid crosslinked carboxymethylcellulose-polyvinyl alcohol hydrogel films for extended release of water soluble basic drugs. *Journal of Drug Delivery Science and Technology,* 52, 421-430.

Gohil, J. M., & Ray, P. (2009). Studies on oxalic acid as a crosslinker of polyvinyl alcohol. *Polymers and Polymer Composites,* 17(7), 403-410.

González, C. G., & Ribes-Greus, A. (2018). Dielectric relaxations and conductivity of cross-linked PVA/SSA/GO composite membranes for fuel cells. *Polymer Testing*, 67, 55-67.

Goodship V and Jacobs D. "Polyvinyl alcohol: materials, processing and applications, (Smithers Rapra Technology, 2009)".

Gulenoor, F., Poddar, P., Bossunia, M. D. I. T., Dafader, N. C., & Chowdhury, S. A. M. (2016). γ-irradiated polyvinyl alcohol (pva) and citric acid blend hydrogels: Swelling and absorption properties. *Chem. Sci. J,* 7, 1000125.

Heydari, M., Moheb, A., Ghiaci, M., & Masoomi, M. (2013). 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*, 128(3), 1640-1651.

Hieu, N. H. (2016). Pervaporation Dehydration of Ethanol with Malic Acid Crosslinked Graphene/Poly (Vinyl Alcohol) Nanocomposite Membranes. *Journal of Membrane and Separation Technology*, 5, 115-120.

Hoare, T. R., & Kohane, D. S. (2008). Hydrogels in drug delivery: Progress and challenges. *Polymer,* 49(8), 1993-2007.

Hrabalikova, M., Holcapkova, P., Suly, P., & Sedlarik, V. (2016). Immobilization of bacteriocin nisin into a poly (vinyl alcohol) polymer matrix crosslinked with nontoxic dicarboxylic acid. *Journal of applied polymer science*, 133(28).

Işıklan, N., & Şanlı, O. (2005). Separation characteristics of acetic acid–water mixtures by pervaporation using poly (vinyl alcohol) membranes modified with malic acid. *Chemical Engineering and Processing: Process Intensification,* 44(9), 1019-1027.

Jayasekara, R., Harding, I., Bowater, I., Christie, G. B., & Lonergan, G. T. (2003). Biodegradation by composting of surface modified starch and PVA blended films. *Journal of Polymers and the Environment,* 11, 49-56.

Khodaverdi, F., Vaziri, A., Javanbakht, M., & Jahanfar, M. (2021). Improvement of PAN separator properties using PVA/malonic acid by electrospinning in lithium ion-batteries. *Journal of Applied Polymer Science,* 138(13), 50088.

Krstić, M., Radojević, M., Stojanović, D., Radojević, V., Uskoković, P., & Ibrić, S. (2017). Formulation and characterization of nanofibers and films with carvedilol prepared by electrospinning and solution casting method. *European Journal of Pharmaceutical Sciences,* 101, 160-166.

Kudoh, Y., Kojima, T., Abe, M., Oota, M., & Yamamoto, T. (2013). Proton conducting membranes consisting of poly (vinyl alcohol) and poly (styrene sulfonic acid): Crosslinking of poly (vinyl alcohol) with and without succinic acid. *Solid State Ionics,* 253, 189-194.

Kumar, A. S., Ghime, D., & Ghosh, P. (2020). Poly (vinyl alcohol)-bonded carbon electrodes for desalination of brackish water using capacitive deionization. *Journal of The Institution of Engineers (India): Series E,* 101, 125-131.

Kumeta, K., Nagashima, I., Matsui, S., & Mizoguchi, K. (2004). Crosslinking of Poly (vinyl alcohol) via Bis (β-hydroxyethyl) Sulfone. *Polymer journal,* 36(6), 472-477.

Liu, T., Peng, X., Chen, Y., Zhang, J., Jiao, C., & Wang, H. (2020). Solid-phase esterification between poly (vinyl alcohol) and malonic acid and its function in toughening hydrogels. *Polymer Chemistry*, 11(29), 4787-4797.

Luo, S., & Netravali, A. N. (2003). A study of physical and mechanical properties of poly (hydroxybutyrate-co-hydroxyvalerate) during composting. *Polymer degradation and stability*, 80(1), 59-66.

Lusiana, R. A., Siswanta, D., Mudasir, M., & Hayashita, T. (2013). The influence of PVA. cl. citric acid/chitosan membrane hydrophicility on the transport of creatinine and urea. *Indonesian Journal of Chemistry,* 13(3), 262-270.

Maitra, J., & Shukla, V. K. (2014). Cross-linking in hydrogels-a review. Am. J. Polym. Sci, 4(2), 25-31.

Maji, P., Gandhi, A., Jana, S., & Maji, N. (2013). Preparation and characterization of maleic anhydride cross-linked chitosan-polyvinyl alcohol hydrogel matrix transdermal patch. *J. Pharma Sci Tech,* 2(2), 62-67.

Majidi, L., Faska, Z., Znini, M., Kharchouf, S., Bouyanzer, A., & Hammouti, B. (2010). Synthesis and anticorrosive effects of epoxy-allylpulegols on steel in molar hydrochloric acid. *J. Mater. Environ. Sci,* 1(4), 219-226.

Marín Cardona, E. S., Rojas Camargo, J., & Ciro Monsalve, Y. A. (2014). A review of polyvinyl alcohol derivatives: promising materials for pharmaceutical & biomedical applications, *Afr. J. Pharm. Pharmacol.* 8(24) 674-684

Nataraj, D., Reddy, R., & Reddy, N. (2020). Crosslinking electrospun poly (vinyl) alcohol fibers with citric acid to impart aqueous stability for medical applications. *European Polymer Journal,* 124, 109484.

Nguyen, D. T., Ly, K. L., Tran, N. M. P., Ho, M. H., Tran, T. T. P., Nguyen, T. H., ... & Vo, V. T. (2019). Effect of Microwave Irradiation on Polyvinyl Alcohol as a Carrier of Silver Nanoparticles in Short Exposure Time. *International Journal of Polymer Science*, 2019, 1-4.

Nulik, B. W., & Endarko, E. (2017, January). Performance analysis of carbon electrode synthesized with poly (vinyl alcohol) and citric acid as cross-linking agent for desalination of NaCl solution in capacitive deionization. *In AIP Conference Proceedings* (Vol. 1788, No. 1). AIP Publishing.

Pangon, A., Saesoo, S., Saengkrit, N., Ruktanonchai, U., & Intasanta, V. (2016). Multicarboxylic acids as environment-friendly solvents and in situ crosslinkers for chitosan/PVA nanofibers with tunable physicochemical properties and biocompatibility. *Carbohydrate polymers,* 138, 156-165.

Ponco, A., & Helmiyati, H. (2020, June). Hydrogel of carboxymethyl cellulose and polyvinyl alcohol modified by CuNPs as antibacterial in wound dressing. *In AIP Conference Proceedings* (Vol. 2242, No. 1). AIP Publishing.

Qiu, K., & Netravali, A. N. (2012). Fabrication and characterization of biodegradable composites based on microfibrillated cellulose and polyvinyl alcohol. *Composites Science and Technology,* 72(13), 1588-1594.

Qiu, K., & Netravali, A. N. (2013). A composting study of membrane-like polyvinyl alcohol based resins and nanocomposites. *Journal of Polymers and the Environment*, 21, 658-674.

Qiu, K., & Netravali, A. N. (2013). Halloysite nanotube reinforced biodegradable nanocomposites using noncrosslinked and malonic acid crosslinked polyvinyl alcohol. *Polymer composites,* 34(5), 799-809.

Quan, P., Wan, X., Tian, Q., Liu, C., & Fang, L. (2020). Dicarboxylic acid as a linker to improve the content of amorphous drug in drug-in-polymer film: Effects of molecular mobility, electrical conductivity and intermolecular interactions. *Journal of Controlled Release,* 317, 142-153.

Reddy, N., Reddy, R., & Jiang, Q. (2015). Crosslinking biopolymers for biomedical applications. *Trends in biotechnology,* 33(6), 362-369.

Riyajan, S. A., Chaiponban, S., & Tanbumrung, K. (2009). Investigation of the preparation and physical properties of a novel semi-interpenetrating polymer network based on epoxised NR and PVA using maleic acid as the crosslinking agent. *Chemical Engineering Journal,* 153(1-3), 199-205.

Rohatgi, C. V., Dutta, N. K., & Choudhury, N. R. (2015). Separator membrane from crosslinked poly (vinyl alcohol) and poly (methyl vinyl ether-alt-maleic anhydride). *Nanomaterials,* 5(2), 398-414.

Sabzi, M., Afshari, M. J., Babaahmadi, M., & Shafagh, N. (2020). pH-dependent swelling and antibiotic release from citric acid crosslinked poly (vinyl alcohol)(PVA)/nano silver hydrogels. *Colloids and Surfaces B: Biointerfaces,* 188, 110757.

Salgado, D. C., & Palacios, J. A. (2020). Poly (vinyl alcohol) membranes cross-linked with maleic anhydride and 2, 5-furandicarboxylic acid: conventional heating and microwave irradiation. *ChemistrySelect,* 5(16), 4826-4838.

Samnani, M., Rathod, H., & Raval, H. (2018). A novel reverse osmosis membrane modified by polyvinyl alcohol with maleic anhydride crosslinking. *Materials Research Express,* 5(3), 035304.

Sanchez, L. M., & Alvarez, V. A. (2019). Development of potentially biocompatible hydrogels with cylindrical pores prepared from polyvinyl alcohol and low-molecular weight polyacrylic acid. *Polymer Engineering & Science,* 59(7), 1479-1488.

Sapalidis, A. A. (2020). Porous Polyvinyl alcohol membranes: Preparation methods and applications. *Symmetry,* 12(6), 960.

Saraf, A., Johnson, K., & Lind, M. L. (2014). Poly (vinyl) alcohol coating of the support layer of reverse osmosis membranes to enhance performance in forward osmosis. *Desalination,* 333(1), 1-9.

Saxena SJPA., 61st JECFA: FAO. *Chemical and Technical Assessment.* (2004).

Solaro, R., Corti, A., & Chiellini, E. (2000). Biodegradation of poly (vinyl alcohol) with different molecular weights and degree of hydrolysis. *Polymers for Advanced Technologies,* 11(8-12), 873-878.

Song, J., Wang, X., & Chang, C. T. (2014). Preparation and characterization of graphene oxide. *Journal of Nanomaterials*, 2014.

Sonker, A. K., & Verma, V. (2018). Influence of crosslinking methods toward poly (vinyl alcohol) properties: Microwave irradiation and conventional heating. *Journal of Applied Polymer Science*, 135(14), 46125.

Sonker, A. K., Rathore, K., Nagarale, R. K., & Verma, V. (2018). Crosslinking of polyvinyl alcohol (PVA) and effect of crosslinker shape (aliphatic and aromatic) thereof. *Journal of Polymers and the Environment,* 26, 1782-1794.

Sonker, A. K., Rathore, K., Teotia, A. K., Kumar, A., & Verma, V. (2019). Rapid synthesis of high strength cellulose–poly (vinyl alcohol)(PVA) biocompatible composite films via microwave crosslinking. *Journal of Applied Polymer Science,* 136(17), 47393.

Sonker, A. K., Tiwari, N., Nagarale, R. K., & Verma, V. (2016). Synergistic effect of cellulose nanowhiskers reinforcement and dicarboxylic acids crosslinking towards polyvinyl alcohol properties. *Journal of Polymer Science Part A: Polymer Chemistry, 54*(16), 2515-2525.

Suganthi, S., Mohanapriya, S., Raj, V., Kanaga, S., Dhandapani, R., Vignesh, S., & Kalyana Sundar, J. (2018). Tunable physicochemical and bactericidal activity of multicarboxylic-acids-crosslinked polyvinyl alcohol membrane for food packaging applications. *ChemistrySelect,* 3(40), 11167-11176.

Suganthi, S., Vignesh, S., Kalyana Sundar, J., & Raj, V. (2020). Fabrication of PVA polymer films with improved antibacterial activity by fine-tuning via organic acids for food packaging applications. *Applied Water Science,* 10(4), 1-11.

Tran, H. L., Van, L. T. M., Vuu, M. N. D., & Mai, P. T. (2016). Separation performance of poly (vinyl alcohol) based nanofiltration membranes crosslinked by malic acid for salt solutions. *VNUHCM Journal of Science and Technology Development,* 19(3), 70-78.

Tran, H. L., Vuu, M. N. D., Hoang, Q. M., Nguyen, N. T., & Mai, P. T. (2016). Pervaporation dehydration of ethanol-water mixture using crosslinked poly (vinyl alcohol) membranes. *VNUHCM Journal of Science and Technology Development*, 19(4), 97-106.

Truong, Y. B., Choi, J., Mardel, J., Gao, Y., Maisch, S., Musameh, M., & Kyratzis, I. L. (2017). Functional Cross-Linked Electrospun Polyvinyl Alcohol Membranes and Their Potential Applications. *Macromolecular Materials and Engineering,* 302(8), 1700024.

Valdes, O., Ávila-Salas, F., Marican, A., Fuentealba, N., Villasenor, J., Arenas-Salinas, M., ... & Durán-Lara, E. F. (2018). Methamidophos removal from aqueous solutions using a super adsorbent based on crosslinked poly (vinyl alcohol) hydrogel. *Journal of Applied Polymer Science,* 135(11), 45964.

Velutheril Thomas, L., & Nair, P. D. (2019). An electrospun citric acid modified polyvinyl alcohol scaffold for vascular tissue engineering. *Journal of Bioactive and Compatible Polymers,* 34(3), 263-279.

Vijayalakshmi, S. P., & Madras, G. (2006). Effects of the pH, concentration, and solvents on the ultrasonic degradation of poly (vinyl alcohol). *Journal of applied polymer science,* 100(6), 4888-4892.

Wang, N., Si, Y., Yu, J., Fong, H., & Ding, B. (2017). Nano-fiber/net structured PVA membrane: effects of formic acid as solvent and crosslinking agent on solution properties and membrane morphological structures. *Materials & Design*, 120, 135-143.

Wang, S., Ren, J., Li, W., Sun, R., & Liu, S. (2014). Properties of polyvinyl alcohol/xylan composite films with citric acid. *Carbohydrate polymers*, 103, 94-99.

Wilson D. S. Georgia Institute of Technology, (2011), PhD Thesis.

Xie, Z., Hoang, M., Duong, T., Ng, D., Dao, B., & Gray, S. (2011). Sol–gel derived poly (vinyl alcohol)/maleic acid/silica hybrid membrane for desalination by pervaporation. *Journal of Membrane Science,* 383(1-2), 96-103.

Xu, S., Shen, L., Li, C., & Wang, Y. (2018). Properties and pervaporation performance of poly (vinyl alcohol) membranes crosslinked with various dianhydrides. *Journal of Applied Polymer Science*, 135(17), 46159.

Xue, J., Wu, T., Dai, Y., & Xia, Y. (2019). Electrospinning and electrospun nanofibers: Methods, materials, and applications. *Chemical reviews,* 119(8), 5298-5415.

Xue, Y. L., Huang, J., Lau, C. H., Cao, B., & Li, P. (2020). Tailoring the molecular structure of crosslinked polymers for pervaporation desalination. *Nature communications*, 11(1), 1461.

Xue, Y. L., Lau, C. H., Cao, B., & Li, P. (2019). Elucidating the impact of polymer crosslinking and fixed carrier on enhanced water transport during desalination using pervaporation membranes. *Journal of Membrane Science*, 575, 135-146.

Yoon, J. Y., Zhang, H., Kim, Y. K., Harbottle, D., & Lee, J. W. (2019). A high-strength polyvinyl alcohol hydrogel membrane crosslinked by sulfosuccinic acid for strontium removal via filtration. *Journal of Environmental Chemical Engineering*, 7(1), 102824.

Zhang, R., Liang, B., Qu, T., Cao, B., & Li, P. (2019). High-performance sulfosuccinic acid cross-linked PVA composite pervaporation membrane for desalination. *Environmental technology,* 40(3), 312-320.

Zhao, B., Lu, C. H., & Liang, M. (2007). Solvent-free esterification of poly (vinyl alcohol) and maleic anhydride through mechanochemical reaction. *Chinese Chemical Letters,* 18(11), 1353-1356.

Zhu, M., Hua, D., Zhong, M., Zhang, L., Wang, F., Gao, B., ... & Huang, C. (2018). Antibacterial and effective air filtration membranes by "green" electrospinning and citric acid crosslinking. *Colloid and Interface Science Communications,* 23, 52-58.

(2023) ; http://www.jmaterenvironsci.com