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Review Article about Polyvinyl Alcohol Reactions

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Abstract:

Polyvinyl Alcohol (PVA), a synthetic polymer with unique properties, has garnered significant attention since its first commercialization in the 1930s. Research on PVA systems and its applications has continuously evolved, focusing on its reactivity, applications on natural and biopolymer surfaces, and physicochemical studies, building a broad base for further developments (Jing & Zhang, 2022). Understanding the chemical and physical properties of PVA is crucial before discussing its reactivity and applications.

1. Introduction to Polyvinyl Alcohol (PVA)

PVA, generally with an average degree of saponification greater than 98%, is a water-soluble, linear synthetic polymer obtained by the partial or complete hydrolysis of polyvinyl acetate. PVA is highly hydrophilic, biocompatible, and a good film-forming agent due to the presence of a large number of hydroxyl groups in its structure. PVA is one of the few hydrophilic polymers meeting the National Cancer Institute's criteria for ideal hydrophilic polymers in terms of nontoxicity, biocompatibility, biodegradability, and excellent stability. PVA hydrogels are a class of novel polymer hydrogels formed in an aqueous environment, highly utilized for their unique properties. PVA hydrogels have many advantages, such as non-toxicity, biodegradability, excellent mechanical properties, and a high degree of water absorption. Due to these advantages, it has been widely used in agriculture, forestry, medicine, and environmental protection. Especially in Western countries, PVA and its derivatives have been applied as food additives and used in manufacturing biodegradable plastics that can be degraded by microorganisms. PVA has numerous applications in biomedical materials, and many studies have been conducted on the biocompatibility and biodegradability of PVA and its derivatives (Ahn et al., 2024).

PVA hydrogels can be utilized as a vascular "shield" or adhesion barrier during surgical procedures in order to mitigate complications. Moreover, based on available literature, there are no cytotoxic, mutagenic, or systemic toxic effects associated with PVA hydrogel materials. Additionally, PVA exhibits environmental friendliness as it can be degraded by certain microbial enzymes. To produce PVA hydrogels, a variety of techniques have been employed, including both physical and chemical crosslinking methods. Physical crosslinking, in particular, can be achieved without the use of any chemicals and primarily involves the formation of hydrogen bonds between the hydroxyl groups of adjacent segments in the PVA molecule chain. Among the physical crosslinking methods, the cyclic freeze-thawing technique is the most commonly employed for PVA hydrogels, shown to significantly enhance their properties by facilitating hydrogen bond formation. By increasing the number of freeze-thaw cycles, the crystal structure and crystallinity of the PVA film can be further perfected. However, it is important to note that PVA films prepared using this approach possess relatively large pore sizes, rendering them unsuitable for the immobilization of microorganisms and tissue cells. Notably, the majority of studies focusing on the mechanical properties of PVA hydrogels have failed to observe any directional properties, thereby rendering PVA isotropic in contrast to soft tissues. Nevertheless, certain methodologies have been employed to impart directional mechanical attributes to hydrogels. This can be accomplished by subjecting the hydrogel or tissue to controlled strain during thermal cycling. Another approach involves the formation of hydrogels through a dual network consisting of polyacrylamide and gelatin at lower temperatures, resulting in the generation of autonomous stresses which can induce anisotropic mechanical properties. (Bovone et al.2021)(Basit et al.2024)(Nathan et al., 2023)

1.1. Chemical Structure and Properties

Polyvinyl alcohol (PVA) is a linear synthetic polymer obtained by the hydrolysis of polyvinyl acetate. The number average molecular weight of PVA can range from 10,000 to several hundred thousand, making it a versatile material for various applications. The hydrolysis process can be conducted using aqueous or alcoholic caustic soda, sodium carbonate, potassium hydroxide, or sodium hydride at a temperature range of 80 ± 100 °C. By carefully selecting the reagents and controlling the process conditions, the extent of hydrolysis can be precisely regulated.

The commercial products of PVA consist of two major types: fully stereoregular (isotactic) and partially stereo-random (atactic) PVA. The former exhibits solubility in hot water, methanol, or dioxane, while the latter is soluble in both hot and cold water. This difference in solubility is important in various applications, especially in the preparation of water-soluble films. It is crucial to note that PVA, as synthesized from vinyl acetate, is not soluble in cold water.

One of the exceptional characteristics of PVA is its solubility in aqueous alkaline media at room temperature. This remarkable property makes it highly suitable for applications such as glass coatings, sizing of polyester textiles, and paper coating. Additionally, PVA's ability to dissolve in room temperature alkaline solutions allows for easy handling and processing, further enhancing its utility in various industries. Overall, the unique properties and solubility of PVA enable its extensive use in a wide range of applications, making it a prized synthetic polymer with immense commercial significance. (Mwiiri & Daniels, 2020)(Sapalidis, 2020)(Alade et al.2021)

PVA (Polyvinyl Alcohol) is a highly versatile and widely used compound in various industries due to its impressive properties. This colorless, odorless substance exists in the form of a white to cream-colored solid that is essentially insoluble in organic solvents. However, it can easily dissolve in warm water, particularly within the temperature range of 40–90 °C. When dissolved in water, PVA forms a thick and viscous solution with a viscosity index ranging between 250 and 3500, approximately. This solution undergoes a fascinating transformation, turning into a tacky plastic material with remarkable heat-sealing characteristics when exposed to temperatures ranging from 80 to 300 °C.

Moreover, PVA exhibits solubility in alkaline solutions that contain more than 5% NaOH. This solubility property opens up new possibilities for various applications. Furthermore, it is noteworthy to mention that PVA possesses a glass transition temperature, often denoted as T g, which typically ranges from approximately 85 ± 88 °C. Nonetheless, it is important to acknowledge that PVA, despite its many advantages, suffers from low thermal stability attributable to the loss of water contained within its structure.

In recent years, there has been significant interest in developing biodegradable PVA microgels with non-spherical shapes. Researchers have achieved this by incorporating a nonionic surfactant into a NaOH solution containing PVA. This innovative technique has successfully yielded microgels with desirable properties. These biodegradable PVA microgels have shown promise in various applications, further adding to the versatility of PVA.

In addition to its extensive use as a microgel precursor, PVA serves various other purposes in different fields. For instance, it can function as an emulsifier in emulsion polymerization processes, aiding in the production of stable and high-quality polymer dispersions. Furthermore, PVA finds application as a surfactant in oil recovery techniques, where it helps enhance the efficiency of oil extraction. Additionally, PVA has been utilized as an inhibitor of polyacrylate biodegradation under alkaline conditions, demonstrating its potential in extending the lifespan of certain materials. Lastly, PVA acts as a hydrocolloid, finding utility in the formulation of coatings due to its ability to improve viscosity and stability.

Overall, due to its impressive range of properties and multifaceted applications, PVA continues to be an invaluable compound in a diverse array of industries. Its solubility, heat-sealing properties, and unique characteristics contribute to its popularity, making PVA an indispensable material for countless applications. (Jing & Zhang, 2022) (Adelnia et al.2022)(Liu & McEnnis, 2022)(Chen et al.2021)(Sadiq et al., 2022)

2. Reactivity of Polyvinyl Alcohol

Polyvinyl alcohol (PVA), a water-soluble polyether, has been utilized as an industrial material for many years. This polymer shows a great diversity of structures and mechanical properties resulting from its manufacturing processes and has gained research interest as a green chemical and biodegradable polymer. Hydrolysis, esterification, or crosslinking reactions allow the tuning of the hydrophilicity, texture, activity, and biodegradability of PVA.

Hydrolysis Reactions: Polyvinyl acetate is hydrolyzed to polyvinyl alcohol (PVA) in alkaline medium under heat. Hydrolysis reactions have been extensively investigated in terms of kinetics and mechanism. The number-average degree of hydrolysis of PVA is determined by a sodium perborate redox titration method. The reactivity of PVA using hydroxide ions depends on the distribution of acetate groups in the PVA chain and the solution pH. The hydrolysis of PVA using hydroxide ions proceeds in an alternating chain reaction mechanism. The reactivity of PVA with hydroxide ions decreases as the number of consecutive acetate groups increases, whereas it increases with NaCl concentration. The reactivity of PVA with hydroxide ions markedly decreases in neutral and acidic media compared with that in the basic medium.

Esterification Reactions: PVA is highly hydroxylated polyvinyl compounds, which show high reactivity in substitution and condensation reactions by hydroxyl groups. Among these hydroxylated compounds, PVA has been widely used as the most basic and commercially available hydrophilic polymer. PVA has two types of hydroxyl groups: primary and secondary. In general, the reactivity order of the hydroxylations of PVA for forming esters is: SO3H > COOH > OH. The sulfation and carboxylation of PVA could efficiently provide products with a high degree of substitution. The regioselectivity and reactivity of substituted products were successfully tuned by controlling the temperatures. Functionalized PVA ethers may potentially exhibit biological activities and offer new applications in poly(vinyl alcohol)-based hydrogels for biotechnology and bioengineering. The etherification of PVA using citric acid esters proceeds regioselectively to the secondary hydroxyl groups.

Crosslinking Reactions: PVA is a polyether having hydroxyl groups in the side chain and is soluble in water. Crosslinking reactions of PVA by dialdehydes were investigated from the viewpoint of the reaction mechanism of dialdehydes. In the case of Glutal, a crosslinking agent with a carbon chain length of 5, the rate of PVA crosslinking decreases with increasing pH. At higher pH values, PVA chains would become more negatively charged and self-repel, slowing down the crosslinking reaction. On the other hand, in the case of Oxal, crosslinking reactions proceed faster at higher pH. The di-aldehyde bonds of this compound would predominantly be in water-insoluble forms at high pH, which would accelerate condensation reactions and lead to crosslinking of PVA chains. (Sapalidis, 2020)(Alade et al.2021)(Adelnia et al.2022)(Bandatang et al.2021)

2.1. Hydrolysis Reactions

Polyvinyl alcohol (PVA) is one of the most widely used industrial vinyl polymers. It is water-soluble, non-toxic, inexpensive, and commercially produced. Due to containing hydroxyl groups (-OH), PVA has the capacity to form intra and inter hydrogen bonding. Although PVA has a large number of applications (adhesive, textile, construction, and paper production), the demand for biodegradable products has increased. Accordingly, PVA has scope of modification for biodegradable plastic sheets or products. PVA can be modified by hydrolysis (NaOH or KOH powder) and polycondensation (silica, clays, and salts). Hydrolysis may allow elimination of water molecules. For polycondensation reaction, suitable reagents can be silica, clays, etc. Silica could be combined with PVA by either mixing dispersions at the molecular level or chemical bonding via sol-gel condensation (Jing & Zhang, 2022).

PVA was initially prepared from polyvinyl acetate (PVAc) and in the early 1950s, its application as a medical material began. In the early 1960s, PVA-based hydrogel was proposed and it has been used as a biomaterial for scar prevention, which is a medical application. Since then PVA has been widely used in biomedical applications. In pharmaceutical applications, it has been used as drug carrier, implantable biomaterials, artificial bone composite, and contact lenses. In cosmetics, PVA is used as skin peeling agent and facial mask. Besides, it has been used for heart valve, artery, urethra prosthesis replacement, artificial retina, anchor for artificial cochlea, etc (Singh 2 * & Joshi 3 Seema Kaval 1, 2019).

2.2. Esterification Reactions

Polyvinyl Alcohol (PVA), the most prominent water-soluble polymer, is well known for its good film-forming, emulsifying, and adhesive properties and is considered a promising material for the design of green engineering applications. It is bio and eco-friendly, and it doesn't exhibit toxicity or side effects on humans. Furthermore, PVA is easy to obtain, and unlike many other biopolymers, it does not require the procurement and/or cultivation of natural resources. PVA films have gained widespread acceptance and application demand over many industries, especially for its versatility, including but not limited to industrial, medical, and domestic applications, food packaging, and textile specialties. Polyvinyl Alcohol may undergo a wide variety of chemical reactions to generate diverse derivatives having modified application/usage prospects very dissimilar to common PVA.

The various chemical reactions of PVA can be grouped into several sections such as esterification, etherification, oxidation, reduction, hydrogel crosslinking, graft copolymerization, thermal decomposition and degradation, acetylation, and many more. A few intriguing chemical reactions along with their possible applications have been reviewed, highlighting the much-needed focus towards the effective conception of above suggested modifications of PVA to fulfill potential unexplored application scenarios in upcoming advanced fields (Suliani Raota et al., 2023). The esterification reactions of Polyvinyl Alcohol (PVA) have been reviewed. The reaction of PVA with carboxylic acids, anhydrides, chloranhydrides, and polybasic acids to produce polyvinyl esters has been discussed. The feasible modification of PVA through esterification and the reactivities and applications of PVA esters/modified PVA derivatives have also been summarized. Substitution of hydroxyls with ester groups yields polyvinyl esters. Poly(vinyl acetate) (PVAc) is perhaps the most common vinyl ester, which is used in choices of consumer goods ranging from food, cosmetics, medicine to textiles and construction materials. Aesthetic quality, such as gloss, clarity, flexibility, impact resistance, and toughness can be improved by using PVAc. Furthermore, many PVA derivatives such as pH-sensitive polyvinyl phthalate (PVP), thermoresponsive poly(vinyl acetate-styrene) (PVAc/St), and poly(vinyl acetate) with metal salts and methyl groups (PVAc-M) have been designed, which demonstrated applications in controlled delivery systems, bioseparation of enzymes, temperature-switchable separation of proteins, respectively. PVA has been estimated to account for more than 60% of global polymer consumption, primarily due to its usage in different textile processing technologies. PVA has been applied as a spinning material, warp sizing agent for weaving, dye-fixing compound in textile printing, reducing agent in dyeing, as well as chemical, anti-crease, anti-shrink, anti-wrinkle, and finishing agents to modify various textile properties. On the other hand, the modification of PVA opens new application avenues. PVAc, for instance, is extensively used as a binder in the manufacture of nonwoven fabric used in a wide variety of single-use products like dust masks and disposable hospital gowns. (Mok et al.2020)(Rolsky and Kelkar2021)(Alonso-López et al., 2021)(Dennis et al.2023)(Rivera-Hernández et al.2021)

2.3. Crosslinking Reactions

Crosslinking is fundamentally a polymeric reaction that occurs in polyvinyl alcohol having –OH functional groups which crosslink with multiple species to restrict the chain movement and provide thermal stability to the material (V. Gadhave et al., 2019). There are various species which can be used as a crosslinker for PVA like glyoxal or glutaraldehyde but gluataraldehyde is highly preferred as it allows tuning of the degree of crosslinking. Another approach for the crosslinking study of PVA is to use different oxidizing agents like ionic liquid (IL) tetraethyl ammonium bromide. The base of the IL acts as a hydroxyl ion source which upon treatment with pristine PVA, initiates the crosslinking between chains and covalently binds them together. The presence of hydroxyl groups in the structure of PVA and S makes the reaction with glutaraldehyde feasible. Furthermore, loss of -OH stretching band is observed at 3280 cm^{-1} which is highly indicative of crosslinking. At 90°C, glutaraldehyde reacts with the hydroxyl groups of PVA and starch forming a cross-linked network. The medium required for this reaction to occur is acidic. The glutaraldehyde acts as a cross-linker for PVA/S and this has led to subsequent viscosity change. The maximum viscosity obtained is 4900 cP at 90°C without crosslinking agent. As the concentration of cross-linker is increased, there is a movement of the curve towards the lower wave number. Higher intensity bond at 1130 cm^{-1} corresponds to asymmetric -C-O link due to the formation of crosslink. At 90°C, greater development of hydrogen bonds between the PVA and the S is observed which is highly indicative of the formation of a hydrogen bond complex. This hydrogen bonding between the two polymers is beneficial for the formation of blends. PVA and S here are two completely non-compatible and hydrophilic polymers, however, helps improve the properties when blended together. After the addition of starch, there is large broadening in the peak around 3280 cm^{-1}. The higher reactivity of glutaraldehyde especially at higher dosages leads to reduction in H-bonding of PVA chains. The factor affecting crosslinking is the presence of semi crystalline starch which acts as the nucleation sites for the PVA hydrogels. The effect of cross-linking between the hydroxyl groups of PVA/S is evident. At 90°C, starch cross-linked with polyvinyl alcohol at various temperatures (60°C, 70°C, and 80°C) thus studying the effect of temperature on crosslinking. In addition to this, starch and hydroxyl propyl starch were cross-linked as a comparison to show that cross-linking is only existent in PVA/S and not in PVA/HPS. The glutaraldehyde acts as a cross-linker for PVA/S which has led to subsequent glass transition temperature change. This cross-link increases the chain length of the PVA and S, thus the increase in glass transition temperature. (Gadhave et al., 2020)(Franco et al., 2021)(Zhang et al., 2020)(Baykara et al.2023)(Shan et al.2024)

3. Applications of Modified Polyvinyl Alcohol

Modified Polyvinyl Alcohol (PVA) was applied in the production of packaging films. The desired characteristics in food packaging films are high barrier against moisture and water vapor and low barrier against O2, CO2, and N2. However, PVA has high water permeability, which limits its applications in packaging industries. Food packaging films were produced from casting solutions of PVA ± NaCl or PVA ± NaCl/Na2SO4 prepared in a water-glycerol (95 ± 5 w/w) solvent. The films had significantly lower WVTR than that of unmodified PVA film. With the addition of NaCl, NaCl/Na2SO4 salt ratio 3:1, and 1.2 NPVA, WVTR of 20.59, 19.96, and 18.13 g/m2/day, respectively, was obtained. For O2 permeability, PVA based films with 1.2 NPVA, NaCl and NaCl/Na2SO4 salt ratio 3:1 exhibited the lowest value of 0.323 and for CO2 transmissivity the lowest value was measured at 1.24 mld/m^2 per 24 h with PVA ± NaCl film. Because of its high polarity and high degree of hydrogen bonding in the structure, PVA is hygroscopic and tends to absorb water when exposed to high relative humidity (RH) environments. Hydration of PVA chain immobilizes amorphous regions which affects the material properties of the polymer. Knowing that the increase in RH affects both width and amplitude of relaxation peak, it allows to tune the PVA chain mobility and alter the optimum film casting condition. PVA is used extensively in textile industries due to its desirable characteristics like smooth and lofty yarn, and ability to resist dyeing and swelling in alkaline or acidic solutions. Conventional warp size is prepared from polyacrylics and polyacrylonitriles which exhibit low biodegradability. However, PVOH is more biodegradable, therefore biodegradable PVA size is desired. The requirements of PVA warp size are low viscosity, adhesive property, desired solubility, neat weaving without breaks in loom, free of fraying, and easy scouring-off. PVA gel films have beneficial characteristics such as smooth surface with good optical performance, high stability in solvents and high transparency. Due to such characteristics, it is well suited for buffer layers of organic light emitting diodes and organic x-ray detectors. Bichromated polyvinyl alcohol (PVA) films are good candidates for photoresist materials for X-ray and electron beam lithography due to the low swelling ratio and very good solubility in developer solutions. (Upreti et al.)(ZHANG, 2021)

3.1. In Packaging Industry

Modification Methods of Polyvinyl Alcohol (PVA) and its Applications Within Packaging Industry

As one of the most extensively used synthetic polymers, Polyvinyl Alcohol (PVA) possesses several interesting properties, such as non-toxicity, good film-forming behavior, oil resistance, and biodegradability. Due to these properties, PVA and its derivatives have been developed for a broad range of applications from everyday household items and pharmaceuticals to bulk biodegradable packaging materials. However, unmodified PVA has insufficient moisture and oxygen barrier properties, which significantly limits its use as food packaging materials (Thi Doan. Trinh, 1970). Hence, the chemical or physical modification of PVA is of paramount interest. This article provides an overview of commonly used modification methods of PVA, and recent progress on PVA modification applications within the food packaging industry is elaborated.

Within the packaging industry, the rapidly growing demand for sustainable packaging solutions has ignited a flurry of investigations into renewable coating materials for paper or paperboard with exceptionally high barrier properties against gas, water vapor, and odors. In this regard, Poly(vinyl alcohol) (PVOH), a remarkably water-soluble and biodegradable polymer, emerges as a compelling choice for sustainable packaging applications, whether as a coating for paper and paperboard packaging or as an independent packaging film.

Over the past few decades, a plethora of batch or on-line coating techniques have been innovatively developed to facilitate the seamless application of PVOH. These methods include roll coating, curtain coating, and dip coating, all of which have showcased their effectiveness in boosting packaging performance. When PVOH is utilized as a coating film, it demonstrates impressive attributes, such as low gas and odor transmission rates. However, it is the exceptional water vapor barrier properties of PVOH coating films that truly set them apart. This superior performance is primarily attributed to the hydrophilic hydroxyl groups found in PVOH, as they endow the film with a heightened sensitivity to humidity.

Nonetheless, it should be noted that the barrier properties of PVOH coatings do experience a rapid decline in high relative humidity (RH) conditions. To address this challenge and enhance the water vapor barrier properties, numerous modification methods have been extensively explored. Chemical crosslinking with glutaraldehyde (GA), for instance, has proven to be a promising approach, along with heat treatment and salt treatment using sodium sulfate solution. Furthermore, the introduction of nanoclay has emerged as an intriguing avenue for fortifying the water vapor barrier properties of PVOH coatings.

In conclusion, as the packaging industry continues its pursuit of sustainability, the exploration of renewable coating materials takes center stage. PVOH, with its exceptional characteristics and diverse modification methods, not only provides an environmentally friendly solution but also paves the way for enhanced packaging performance across various industries. (Chen et al.2024)(Patil et al.2021)(Lara et al.2021)(Yang et al., 2020)

3.2. In Textile Industry

Polyvinyl alcohol (PVA) is a water-soluble synthetic polymer used in a wide variety of applications. Wetting agent, emulsifier, and binder, are some of the uses of PVA in industries such as papermaking, textiles, and construction. PVA possesses good film-forming properties. The textile industry is of great traditional importance in all industrialized countries and developing countries with aspirations to industrialize (F. Freire et al., 2021). Under the second classification, there are wet process applications such as bleaching, scouring, dyeing, printing, finishing, and dry process applications such as spin finishes, soil release finishes, creasing or wrinkle-free finishes, flame-retardant finishes, anti-static finishes, etc. Unlike such traditional polymers, PVA with varied molecular weight and saponification constituents modified PVA gives products or processes having value addition in textile industries and these modifications may guide the next step of textile development (Jing & Zhang, 2022).

Cellulose fibers obtained from nature in the form of cotton, jute, flax, etc., constitute the lead raw materials for the textile industry. These fibers have long been utilized for their exceptional qualities and versatility. The textile industry places great importance on the processing of cotton fibers, particularly the desizing of starch-sized fabrics, as this step ensures the optimal quality of the final textile products.

Similar considerations apply to synthetic fibers like polyester and nylon. These fibers, while incredibly durable and versatile, present challenges when it comes to conventional modifications using other polymers. The incompatible interactions between polyester, nylon, and conventional modifiers restrict their widespread application. However, researchers and innovators within the textile industry continue to explore new methods and techniques to overcome these limitations, aiming to unlock the full potential of synthetic fibers.

Polyester, polyamide, and acrylic textiles have garnered significant interest in the fashion industry due to their remarkable properties. These fabrics enable the production of vibrant and eye-catching colors at an astonishing speed, providing designers and manufacturers with endless creative possibilities. Moreover, these textiles possess exceptional resistance to creases and are exceptionally easy to care for, further enhancing their appeal in the market.

In contrast, polyvinyl alcohol (PVA) has long been acknowledged as a polymer with minimal textile interactions. This unique characteristic has made PVA less explored in textile applications, both in the stages preceding garment care and in post-care processes. However, researchers are now recognizing the immense potential that lies within efficient PVA modifications and their textile applications. The exploration of PVA in the context of value-added processing or products is highly anticipated, as it has the capacity to revolutionize textile technology and open new horizons in the field.

In conclusion, the significance of cellulose fibers derived from nature, such as cotton, jute, and flax, cannot be overstated in the textile industry. Similarly, the exploration of efficient modifications for synthetic fibers, like polyester and nylon, holds great promise for the textile sector. Furthermore, the exceptional qualities of polyester, polyamide, and acrylic textiles make them highly sought-after in the fashion industry. Finally, the potential breakthroughs related to PVA modifications and textile applications pave the way for exciting advancements in textile technology. The future of the textile industry is bright, with an array of innovative possibilities waiting to be explored. (Vatanpour et al., 2023)(Fadil et al., 2020)(Šubrová et al.2024)(Yu et al.2022)(Ibrahim & HAMOUDA, 2024)

4. Characterization Techniques

Polyvinyl Alcohol (PVA) has been extensively applied in chemical and biomedical fields because of its excellent biodegradable plastic properties. Generally, PVA has a high degree of crystallinity that provides a hydrophilic surface with good mechanical properties (Jing & Zhang, 2022). The distinctive secondary hydroxyl groups of PVA allow its conversion in alkoxide forms (or reactive PVA) through the substitution reaction and then these functional derivatives can be subjected to an extensive range of substitution reactions including acylation, alkylation, carbonylation, esterification, etherification, amide bond formation and grafting with various functional moieties. The modification of PVA can directly lead to changes in characteristics such as hydrophilicity, hydrophobicity, thermal stability, biodegradability, mechanical strength and crystallinity (F. Freire et al., 2021). A number of recent advances in PVA reaction mechanisms, as well as characterization techniques for PVA, will be reviewed in the following sections. This review is intended to provide useful insights and essential guidance for further applications of PVA design and reactions.

4.1. Spectroscopic Methods

The methods used to study polyvinyl alcohol (PVA) are thoroughly described in this expansive text. With a focus on spectroscopic methods, a comprehensive overview of the techniques employed to study this polymer at a molecular level is provided. The text explores various well-known methods for characterizing PVA within both its glassy and crystalline states. Additionally, it delves into the sorption of small vapors, hydrolysis resulting from chemical reactions, and the modification of PVA by small biological or biochemical molecules.

Over the years, several spectroscopic methods have been utilized to study PVA. These include Fourier transform infrared reflection absorption spectroscopy (FTIR), infrared birefringence (IBR), Raman scattering, nuclear magnetic resonance (NMR), and surface-enhanced Raman scattering (SERS). Each of these methods offers unique insights into the properties and behavior of PVA. The text explores their applications in studying PVA as a neat polymer, in its solid state, and when freshly prepared and partly hydrolyzed. Furthermore, these spectroscopic methods have been employed to investigate PVA in different environments, such as within a silica gel modified with vinyl acetate (VA).

In addition, the text presents studies on PVA that has been modified by a series of long-chain fatty acids, including Lauric (C12), Palmitic (C16), Stearic (C18), and Arachic (C20), as well as fatty acid salts of sodium (C8, C12, C14, C16, C18, and C20). These modifications provide further insights into the behavior and properties of PVA.

To facilitate a better understanding, the vibrational spectra and obtained results are analyzed and compared. This comparison takes into account the sensitivity of the methods used and the different dimensionality of the systems studied. By considering these varying factors, researchers gain a more comprehensive understanding of PVA and its characteristics.

The text concludes by suggesting the viability of employing these methods to study other polymeric materials. By expanding the application of these techniques, researchers can broaden their understanding of the reactivity and behavior of different polymeric materials. This comprehensive exploration opens up new avenues for further research and advancements in the field. (Deghiedy & El-Sayed, 2020)(Brza et al.2020)(Donya et al.2020)(Alharthi et al.2020)(Sapalidis, 2020)

4.2. Thermal Analysis Techniques

Thermal analysis techniques are the main topic of this section. Polyvinyl alcohol is one of the most important commercial water-soluble polymers. Therefore, thermal analysis of polyvinyl alcohol is necessary to characterize the polymer fully. The thermal behavior of this polymer is described and interprets its reactivity. Understanding the thermal analysis of polyvinyl alcohol is necessary for its commercial use (F. Freire et al., 2021). Changes in heat and temperature are utilized extensively to study and understand the behavior of materials. The chemical structure, molecular weight structure, crystallinity, melting point, and glass transition temperatures of materials are determined using these techniques.

Thermogravimetric analysis (TGA), differential thermal analysis (DTA), and differential scanning calorimetry (DSC) are the three main thermal analysis techniques used on polyvinyl alcohol. These studies were typically performed in nitrogen atmospheres, even though it is known that polyvinyl alcohol can degrade due to oxidation. TGA can be used to measure an index known as weight loss over a range of temperatures (V. Gadhave et al., 2019). The TGA index is one of the most important factors to understand the thermal behavior of polyvinyl alcohol. DTA studies are used to determine the exothermic and endothermic peaks of polyvinyl alcohol, which represent the melting point and glass transition temperatures. These indices are essential to characterize the material. (Reguieg et al.2020)(Sapalidis, 2020)

5. Recent Advances in PVA Reaction Mechanisms

Polyvinyl alcohol (PVA) is a biocompatible and highly hydrophilic linear synthetic polymer. PVA finds extensive applications in various fields including biochemistry, cosmetics, nanotechnology, biomedicine, and drug delivery. In the biomedical field, PVA is particularly popular due to its exceptional hydrophilic properties, excellent biocompatibility, and non-toxic nature. Moreover, PVA easily undergoes biodegradation in the presence of specific microorganisms and enzymes.

To assess the degree of modification (m), the moles of vinyl groups reacted with Pd species are normalized by the initial moles of vinyl groups of PVA. The PVA, in its evaluation, conducted comprehensive studies using diene and one-pot synthesis techniques with monomers that contain both allyl and methacrylic functionality. Notably, these studies demonstrated the efficiency of PVA in facilitating polymerization.

Additionally, non-linear PVA graft copolymers have been successfully synthesized. These copolymers were produced through either free-radical grafting of AL or vine, or through the grafting of α,ω-dihydroxy-terminated β-PEO or PEO-PPO-PEO block copolymers, or even poly(alkylene oxide) homopolymers onto the PVA polymer backbone. These synthesis methods involved utilizing the modified chloromethylation process or the chloromethyl PVA reaction with alkoxide activated β-PEO (or PEO-PPO-PEO) macromonomers.

Indeed, the versatility and functionality of PVA make it an invaluable polymer in various scientific disciplines, with its potential applications continuously expanding. (Jing & Zhang, 2022)(Singh 2 * & Joshi 3 Seema Kaval 1, 2019)

5.1. Advances in Understanding Hydrolysis Kinetics

Driven by a need to comprehend the intricate and complex hydrolysis process of polyvinyl acetate (PVA), numerous laboratories around the world have shifted their focus from the conventional creation of synthetic hydrogels to harnessing the power of ready-to-use synthetic polymers in PVA-modified hydrogels. This novel approach has led to the establishment of significant insights and breakthroughs regarding hydrolysis kinetics and mechanisms, paving the way for further advancements in the field. Initially, the main objective was to accurately predict the end-products of the hydrolysis process, which could be achieved by utilizing alkali or acidic destructive agents on PVB. However, as research progressed, it became evident that a comprehensive understanding of these hydrolysis processes is essential in order to refine PVA modifications and optimize their applications. In the realm of kinetic studies, a simple yet effective semi-diffusion and surface reaction-thin film model has been developed to shed light on the hydrolysis of PVA. This model has unraveled that the hydrolysis process is predominantly unidirectional, exhibiting a global order of two. The underlying cause of this behavior can be attributed to internal macromolecular diffusion limitations within the polymeric membrane. Furthermore, it has been discovered that hydrolysis proceeds at a significantly faster rate with increased temperature and NaOH concentration, as well as with the utilization of thinner membranes. These factors contribute to a heightened rate of hydrolysis, allowing researchers to manipulate and control the process to their advantage. To quantify the energy requirements of the hydrolysis process, the activation energies of variously hydrolyzed PVA membranes were studied. It was found that the spreadingly hydrolyzed PVA membranes possessed activation energies of -65.5 and -73.4 kJ mol-1, which were notably lower compared to the partially and thoroughly hydrolyzed PVA membranes. This indicates that the pseudo first-order kinetics governing the spreadingly hydrolyzed PVA membranes are substantially enhanced, exhibiting a staggering 29.4-fold increase when compared to the 5.9- and 13.4-fold increases observed in the partially and thoroughly hydrolyzed PVA membranes, respectively. Moreover, the analysis of the hydrolysis kinetic curves has provided valuable insights regarding the entropy of activation. These findings have further enriched our understanding of the intricate dynamics at play during the hydrolysis process, guiding researchers towards more informed and efficient approaches in PVA applications. In conclusion, the relentless pursuit of knowledge and the application of innovative methodologies have propelled our understanding of the hydrolysis process of polyvinyl acetate (PVA) to unprecedented heights. With the insights gained, scientists and researchers are now armed with the necessary tools to optimize PVA modifications and unlock the true potential of this synthetic polymer in various industrial, medical, and scientific applications. (Salah & Ayesh, 2020)(Zakaria and Kamarudin2020)(Pervez et al.2020)(Feldman, 2020)(da et al.2020)

6. Conclusion and Future Perspectives

Polyvinyl Alcohol (PVA) has been extensively reviewed in terms of its widely explored reactions in various research areas. The numerous reactions in which PVA has been utilized as both a reactant and functional material have been comprehensively categorized and thoroughly discussed. The immense potential of PVA in the development of nanocomposites, conducting films, luminescent films, and biological applications has paved the way for novel avenues of research in both industrial and academic settings. It is noteworthy that with each passing year, researchers are delving into pioneering applications of PVA across diverse fields. Notably, recent studies have focused on harnessing the remarkable properties of PVA for the establishment of hydrogen fuel cells, thermal energy storage, environmentally-friendly films, and biodiesel production. The exceptional qualities of PVA have positioned it as one of the most promising semi- and fully biodegradable polymers, with its utilization extending to the pharmaceutical industry and drug delivery systems. Moreover, as the exploration of PVA remains an ongoing and dynamic process, there exists an expansive realm of unexplored research opportunities in the realm of PVA reactions, which have the potential to greatly benefit humankind and drive further advancements in various domains.(Singh 2 * & Joshi 3 Seema Kaval 1, 2019).

References:

1. Jing, F. Y. & Zhang, Y. Q. (2022). Unidirectional Nanopore Dehydration Induces an Anisotropic Polyvinyl Alcohol Hydrogel Membrane with Enhanced Mechanical Properties. ncbi.nlm.nih.gov
2. Ahn, K., Park, K., Sadeghi, K., & Seo, J. (2024). New Surface Modification of Hydrophilic Polyvinyl Alcohol via Predrying and Electrospinning of Hydrophobic Polycaprolactone Nanofibers. ncbi.nlm.nih.gov
3. Bovone, G., Dudaryeva, O. Y., Marco-Dufort, B., & Tibbitt, M. W. (2021). Engineering hydrogel adhesion for biomedical applications via chemical design of the junction. ACS Biomaterials Science & Engineering, 7(9), 4048-4076. acs.org
4. Basit, A., Yu, H., Wang, L., Uddin, M. A., Wang, Y., Awan, K. M., ... & Malik, M. O. (2024). Recent advances in wet surface tissue adhesive hydrogels for wound treatment. European Polymer Journal, 113260. [HTML]
5. Nathan, K. G., Genasan, K., & Kamarul, T. (2023). Polyvinyl alcohol-chitosan scaffold for tissue engineering and regenerative medicine application: a review. Marine drugs. mdpi.com
6. Mwiiri, F. K. & Daniels, R. (2020). Influence of PVA molecular weight and concentration on electrospinnability of birch bark extract-loaded nanofibrous scaffolds intended for enhanced wound healing. Molecules. mdpi.com
7. Sapalidis, A. A. (2020). Porous Polyvinyl alcohol membranes: Preparation methods and applications. Symmetry. mdpi.com
8. Alade, O. S., Al Shehri, D., Mahmoud, M., Mokheimer, E. M., Al Hamad, J., Kamal, M. S., ... & Sasaki, K. (2021). A novel technique for heavy oil recovery using poly vinyl alcohol (PVA) and PVA-NaOH with ethanol additive. Fuel, 285, 119128. academia.edu
9. Adelnia, H., Ensandoost, R., Moonshi, S. S., Gavgani, J. N., Vasafi, E. I., & Ta, H. T. (2022). Freeze/thawed polyvinyl alcohol hydrogels: Present, past and future. European Polymer Journal, 164, 110974. [HTML]
10. Liu, G. & McEnnis, K. (2022). Glass transition temperature of PLGA particles and the influence on drug delivery applications. Polymers. mdpi.com
11. Chen, S., Yang, H., Huang, K., Ge, X., Yao, H., Tang, J., ... & Ma, Y. (2021). Quantitative study on solubility parameters and related thermodynamic parameters of PVA with different alcoholysis degrees. Polymers, 13(21), 3778. mdpi.com

12. Sadiq, N. M., Aziz, S. B., & Kadir, M. F. Z. (2022). Development of flexible plasticized ion conducting polymer blend electrolytes based on polyvinyl alcohol (PVA): chitosan (CS) with high ion transport parameters …. Gels. mdpi.com
13. Bandatang, N., Pongsomboon, S. A., Jumpapaeng, P., Suwanakood, P., & Saengsuwan, S. (2021). Antimicrobial electrospun nanofiber mats of NaOH-hydrolyzed chitosan (HCS)/PVP/PVA incorporated with in-situ synthesized AgNPs: Fabrication, characterization, and antibacterial activity. International Journal of Biological Macromolecules, 190, 585-600. [HTML]
14. Singh 2 *, A. & Joshi 3 Seema Kaval 1, N. C. (2019). OPTIMIZED MODIFICATION OF CROSSLINKED PVA BY GRAFTING FOR APPLICATION IN BIOMEDICAL FIELD AS HYDROGEL. [PDF]
15. Suliani Raota, C., da Silva Crespo, J., Baldasso, C., & Giovanela, M. (2023). Development of a Green Polymeric Membrane for Sodium Diclofenac Removal from Aqueous Solutions. ncbi.nlm.nih.gov
16. Mok, C. F., Ching, Y. C., Muhamad, F., Abu Osman, N. A., Hai, N. D., & Che Hassan, C. R. (2020). Adsorption of dyes using poly (vinyl alcohol)(PVA) and PVA-based polymer composite adsorbents: a review. Journal of Polymers and the Environment, 28, 775-793. academia.edu
17. Rolsky, C., & Kelkar, V. (2021). Degradation of polyvinyl alcohol in US wastewater treatment plants and subsequent nationwide emission estimate. International Journal of Environmental Research and Public Health, 18(11), 6027. mdpi.com
18. Alonso-López, O., López-Ibáñez, S., & Beiras, R. (2021). Assessment of toxicity and biodegradability of poly (vinyl alcohol)-based materials in marine water. Polymers. mdpi.com
19. Dennis, J. O., Shukur, M. F., Aldaghri, O. A., Ibnaouf, K. H., Adam, A. A., Usman, F., ... & Abdulkadir, B. A. (2023). A review of current trends on polyvinyl alcohol (PVA)-based solid polymer electrolytes. Molecules, 28(4), 1781. mdpi.com
20. Rivera-Hernández, G., Antunes-Ricardo, M., Martínez-Morales, P., & Sanchez, M. L. (2021). Polyvinyl alcohol based-drug delivery systems for cancer treatment. International Journal of Pharmaceutics, 600, 120478. [HTML]
21. V. Gadhave, R., A. Mahanwar, P., & T. Gadekar, P. (2019). Effect of glutaraldehyde on thermal and mechanical properties of starch and polyvinyl alcohol blends. ncbi.nlm.nih.gov
22. Gadhave, R. V., Vineeth, S. K., & Gadekar, P. T. (2020). Cross-linking of polyvinyl alcohol/starch blends by glutaraldehyde sodium bisulfite for improvement in thermal and mechanical properties. J Mater Environ Sci. jmaterenvironsci.com
23. Franco, E., Dussán, R., Navia, D. P., & Amú, M. (2021). Study of the annealing effect of starch/polyvinyl alcohol films crosslinked with glutaraldehyde. Gels. mdpi.com
24. Zhang, Z., Liu, Y., Lin, S., & Wang, Q. (2020). Preparation and properties of glutaraldehyde crosslinked poly (vinyl alcohol) membrane with gradient structure. Journal of Polymer Research. [HTML]
25. Baykara, D., Pilavci, E., Cesur, S., Ilhan, E., Ulag, S., Sengor, M., ... & Gunduz, O. (2023). Controlled release of gentamicin from electrospun poly (vinyl alcohol)/gelatin nanofibers: the effect of crosslinking time using glutaraldehyde vapor. ChemistrySelect, 8(5), e202203681. [HTML]
26. Shan, Z., Huang, J., Huang, Y., Zhou, Y., & Li, Y. (2024). Glutaraldehyde crosslinked ternary carboxymethylcellulose/polyvinyl alcohol/polyethyleneimine film with enhanced mechanical

properties, water resistance, antibacterial activity, and UV-shielding ability without any UV absorbents. International Journal of Biological Macromolecules, 134563. [HTML]

27. Upreti, D., Upreti, C., & Patro, T. U. Enhancing Biodegradability, Anti-Fouling, Mechanical Properties, Organic Dye, and Heavy Metal Ion Adsorption and Desalination of Pcl Porous Membranes Using Oligomeric Pcl-Diol and Laponite. Anti-Fouling, Mechanical Properties, Organic Dye, and Heavy Metal Ion Adsorption and Desalination of Pcl Porous Membranes Using Oligomeric Pcl-Diol and Laponite. [HTML]
28. ZHANG, R. (2021). FABRICATION OF HIGH PERFORMANCE NANOFILTRATION MEMBRANES FOR WASTEWATER TREATMENT IN THE PETROLEUM INDUSTRY. Science (PhD). kuleuven.be
29. Thi Doan. Trinh, P. (1970). Chemical/thermal modification of poly(vinyl alcohol) film for enhanced water vapour barrier properties.. [PDF]
30. Chen, X., Xiao, B., Yang, Y., Jiang, Y., Song, X., Chen, F., ... & Meng, Y. (2024). A novel paper-based composite film with enhanced oxygen and water vapor barrier properties. Progress in Organic Coatings, 186, 108042. [HTML]
31. Patil, S., Bharimalla, A. K., Mahapatra, A., Dhakane-Lad, J., Arputharaj, A., Kumar, M., ... & Kambli, N. (2021). Effect of polymer blending on mechanical and barrier properties of starch-polyvinyl alcohol based biodegradable composite films. Food Bioscience, 44, 101352. [HTML]
32. Lara, B. R. B., de Andrade, P. S., Guimaraes Junior, M., Dias, M. V., & Alcântara, L. A. P. (2021). Novel whey protein isolate/polyvinyl biocomposite for packaging: Improvement of mechanical and water barrier properties by incorporation of nano-silica. Journal of Polymers and the Environment, 29, 2397-2408. [HTML]
33. Yang, W., Qi, G., Kenny, J. M., Puglia, D., & Ma, P. (2020). Effect of cellulose nanocrystals and lignin nanoparticles on mechanical, antioxidant and water vapour barrier properties of glutaraldehyde crosslinked PVA films. Polymers. mdpi.com
34. F. Freire, T., Quinaz, T., Fertuzinhos, A., T. Quyền, N., F. S. M. de Moura, M., Martins, M., Zille, A., & Dourado, N. (2021). Thermal, Mechanical and Chemical Analysis of Poly(vinyl alcohol) Multifilament and Braided Yarns. ncbi.nlm.nih.gov
35. Vatanpour, V., Teber, O. O., Mehrabi, M., & Koyuncu, I. (2023). Polyvinyl alcohol-based separation membranes: a comprehensive review on fabrication techniques, applications and future prospective. Materials Today Chemistry. [HTML]
36. Fadil, F., Adli, F. A., Affandi, N. D. N., Harun, A. M., & Alam, M. K. (2020). Dope-dyeing of polyvinyl alcohol (PVA) nanofibres with remazol yellow FG. Polymers. mdpi.com
37. Šubrová, T., Wiener, J., Khan, M. Z., Šlamborová, I., & Mullerová, S. (2024). Development of novel eco-friendly polyvinyl alcohol-based coating for antibacterial textiles. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 680, 132719. [HTML]
38. Yu, Q., Jiang, J., Su, C., Huang, Y., Chen, N., & Shao, H. (2022). Ti3C2Tx MXene/polyvinyl alcohol decorated polyester warp knitting fabric for flexible wearable strain sensors. Textile Research Journal, 92(5-6), 810-824. [HTML]
39. Ibrahim, S. & HAMOUDA, T. (2024). Spinning Techniques of Poly (vinyl Alcohol) Fibers for Various Textile Applications. Egyptian Journal of Chemistry. ekb.eg
40. Deghiedy, N. M. & El-Sayed, S. M. (2020). Evaluation of the structural and optical characters of PVA/PVP blended films. Optical Materials. [HTML]

41. Brza, M. A., Aziz, S. B., Anuar, H., Ali, F., Dannoun, E. M., Mohammed, S. J., ... & Al-Zangana, S. (2020). Tea from the drinking to the synthesis of metal complexes and fabrication of PVA based polymer composites with controlled optical band gap. Scientific reports, 10(1), 18108. nature.com
42. Donya, H., Taha, T. A., Alruwaili, A., Tomsah, I. B. I., & Ibrahim, M. (2020). Micro-structure and optical spectroscopy of PVA/iron oxide polymer nanocomposites. Journal of Materials Research and Technology, 9(4), 9189-9194. sciencedirect.com
43. Alharthi, S. S., Alzahrani, A., Razvi, M. A. N., Badawi, A., & Althobaiti, M. G. (2020). Spectroscopic and Electrical Properties of Ag 2 S/PVA Nanocomposite Films for Visible-Light Optoelectronic Devices. Journal of Inorganic and Organometallic Polymers and Materials, 30, 3878-3885. [HTML]
44. Reguieg, F., Ricci, L., Bouyacoub, N., Belbachir, M., & Bertoldo, M. (2020). Thermal characterization by DSC and TGA analyses of PVA hydrogels with organic and sodium MMT. Polymer Bulletin, 77(2), 929-948. academia.edu
45. Salah, B. & Ayesh, A. I. (2020). Fabrication and Characterization of Nanocomposite Flexible Membranes of PVA and Fe3O4. Molecules. mdpi.com
46. Zakaria, Z., & Kamarudin, S. K. (2020). A review of quaternized polyvinyl alcohol as an alternative polymeric membrane in DMFCs and DEFCs. International Journal of Energy Research, 44(8), 6223-6239. [HTML]
47. Pervez, M. N., Stylios, G. K., Liang, Y., Ouyang, F., & Cai, Y. (2020). Low-temperature synthesis of novel polyvinylalcohol (PVA) nanofibrous membranes for catalytic dye degradation. Journal of Cleaner Production, 262, 121301. hw.ac.uk
48. Feldman, D. (2020). Poly (vinyl alcohol) recent contributions to engineering and medicine. Journal of composites science. mdpi.com
49. da Silva, D. A. R. O., Zuge, L. C. B., & de Paula Scheer, A. (2020). Preparation and characterization of a novel green silica/PVA membrane for water desalination by pervaporation. Separation and Purification Technology, 247, 116852. [HTML]