Journal of Materials and Environmental Science
ISSN : 2028-2508
e-ISSN : 2737-890X
CODEN : JMESCN
Copyright © 2023,
University of Mohammed Premier
Oujda Morocco

J. Mater. Environ. Sci., 2023, Volume 14, Issue 05, Page 560-581

http://www.jmaterenvironsci.com

A Comprehensive Review on the Engineering of Biocompatible Polyvinyl Alcohol Composites with Enhanced Properties Using Carbonaceous Fillers

Pawan Kumar Agrawal [1*], Pragya Sharma [1], V.K. Singh [1], Sakshi Chauhan [1]
[1]*Department of Mechanical Engineering, G. B. Pant University of Agriculture & Technology, Pantnagar-263145, India*
**Corresponding author, Email address: agpawan13@gmail.com*

Received *05 May 2023,*
Revised *26 May 2023,*
Accepted *27 May 2023*

Keywords:
- ✓ *Polyvinyl Alcohol,*
- ✓ *Polymer matrix composites,*
- ✓ *Physical & mechanical properties,*
- ✓ *Carbonaceous materials,*
- ✓ *Surface modification*

Citation*: Pawan Kumar Agrawal, Pragya Sharma, V.K. Singh, Sakshi Chauhan (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.*

Abstract: Polyvinyl alcohol (PVA) is a versatile and highly desirable thermoplastic polymer due to its biocompatible, non-toxic, and biodegradable properties. It exhibits exceptional mechanical and thermal properties, making it suitable for multiple fields. However, its hydrophilicity remains a significant disadvantage that researchers have attempted to mitigate through the use of filler materials or cross-linking in PVA-based composites. Studies have investigated the water absorption and mechanical behaviour of PVA composites and emphasized the importance of filler materials in enhancing interfacial adhesion properties. Carbonaceous materials, such as graphite, are beneficial in various applications due to their low energy state and layered crystal structure, but their absence of reactive ion groups limits their interaction with monomers. Researchers have explored various techniques to modify carbonaceous materials to improve their interfacial adhesion properties with polymer matrices. These studies provide insight into the potential applications of PVA and carbonaceous material-based composites and guidance on optimizing their properties through filler material selection and surface modifications. Applications of PVA and its composites, such as drug delivery systems, tissue engineering, biodegradable packaging, and construction materials, are favoured due to their excellent mechanical and chemical properties. This makes them a desirable option for 3D printing applications.

1. Introduction

From stone to plastics, materials undergo a series of steps from extraction to processing to create finished products. Stone is cut and polished for countertops and flooring, while metals require smelting to separate impurities. Plastics are made through a chemical process of polymerization, forming long chains of molecules, and are shaped by casting and moulding. Sustainability is essential throughout the journey. In recent years, due to growing environmental concerns and issues with the recyclability of synthetic non-biodegradable materials, efforts have increased to develop biodegradable or edible films from biopolymers for eco-friendly plastics (Limpan *et al.* 2010; Tabaght *et al.* 2023). The depletion of petroleum resources, along with the toxicity and non-biodegradability of petroleum-based plastics, has led researchers to focus on environmentally friendly alternatives from non-petroleum sources (Zhang *et al.* 2011).

Composites are currently receiving significant attention not only due to the emergence of new types such as nanocomposites and biomedical compounds but also for their potential applications in various industries from aerospace to construction, thanks to their outstanding properties. By carefully combining matrix and filler materials, composites can exhibit even superior properties compared to traditional metallic materials.

Classification of composites

The schematic diagram depicted in **Figure 1** illustrates the classification of composite materials based on the nature of the matrix material. Within this classification, Polymer Matrix Composites (PMCs) have been identified as the focus of investigation for the present study.

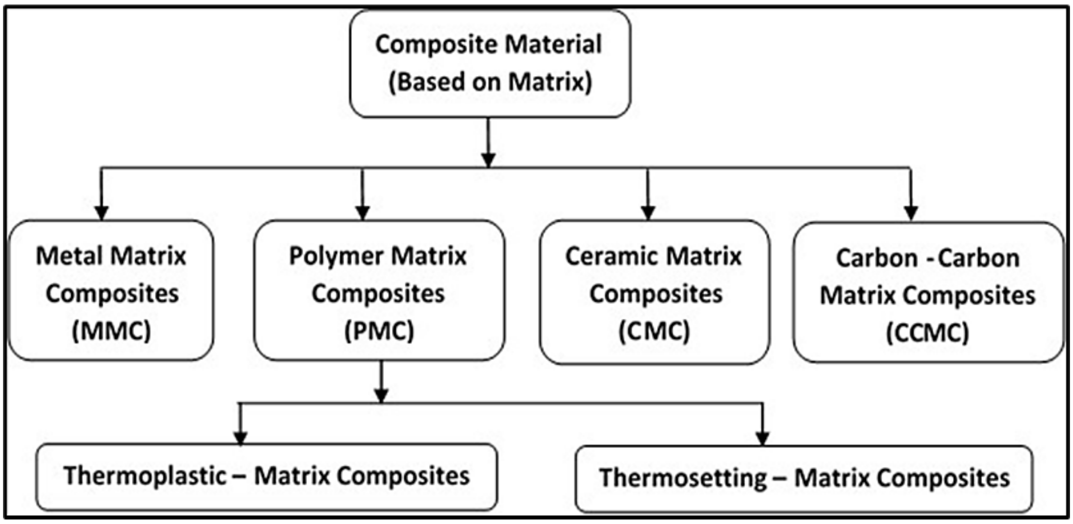

Figure 1. **Classification of composites on the basis of matrix material**

Polymer matrix composites (PMCs) utilize polymers as matrix materials and are widely used in engineering due to their exceptional mechanical and thermal properties. They offer advantages such as high strength-to-weight ratios, low density, low cost, and high abrasion/corrosion resistance. PMCs also exhibit high stiffness and strength along the direction of their reinforcements. PMCs with a low weight reduce fuel consumption, making them suitable for aerospace and automobile applications. In this review paper, PMCs using polyvinyl alcohol (PVA) a thermoplastic as matrix material are studied. Thermoplastic is a plastic composed of polymer resins that soften when heated and harden when cooled, then revert to a soft state when reheated.

The schematic in **Figure 2** categorizes composites based on their filler materials, which greatly impact their properties. This classification is vital in determining the physical and mechanical behavior of composites in various applications.

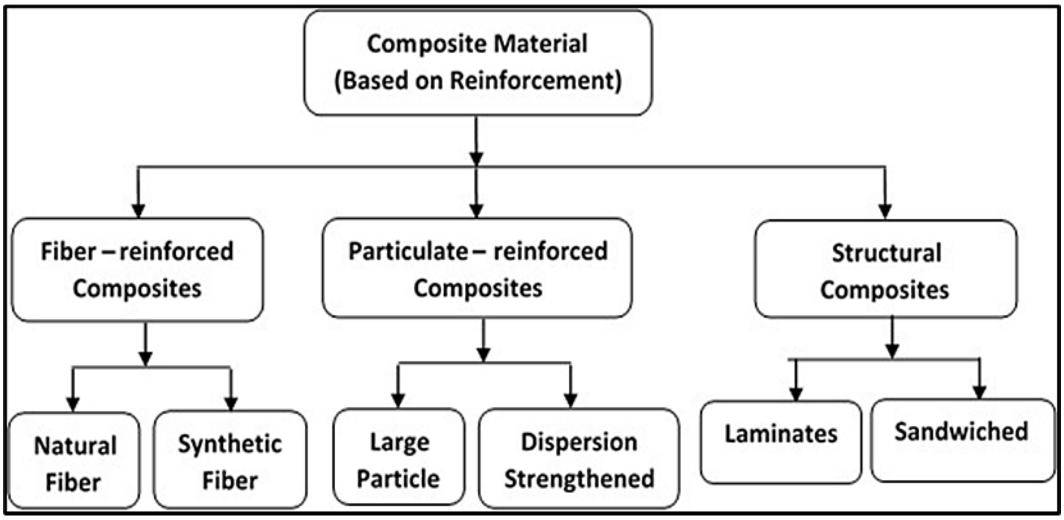

Figure 2. **Classification of composites on the basis of filler material**

Polymers are essential for making nontoxic and biodegradable polymer matrix composites (PMC) to protect the environment. Natural biodegradable polymers include proteins, polysaccharides, and polyesters, while synthetic ones include polyvinyl alcohol, poly anhydrides, and polyamide-an amines. Polyvinyl alcohol (PVA), a water-soluble, non-toxic, and biocompatible semi-crystalline thermoplastic, is eco-friendly and biodegradable (Abdulkhani *et al.* 2013). PVA displays excellent chemical stability and decomposes into CO2 and H2O with the aid of plant-based microorganisms. As it is harmless, biocompatible, and nontoxic, it is commonly used in living organisms. PVA is extensively studied because of its use in nano-filler composite and cross-linked products **(**Nagarkar & Patel 2019**)** and has diverse applications in various fields such as food packaging, medical, tissue engineering, and electronics. PVA is obtained through the hydrolysis of polyvinyl acetate, which is synthesized from vinyl acetate **(**Tsuda, 1963, Nasibi *et al.* 2020**)**. Herman first prepared PVA fibers in 1931 using the wet and dry spinning method for the surgical thread. The physical and functional properties of PVA depend on its degree of hydrolysis and polymerization.

Polyvinyl alcohol (PVA) is a water-soluble polymer, making it suitable for solution casting. PVA possesses impressive tensile strength and pliability, along with resistance to grease, oil, and solvents **(**Watanabe *et al.* 1976**)**. However, exposure to humid environments reduces its tensile strength while increasing elongation **(**Tang & Alavi 2011**)**. PVA's easy processability, good mechanical properties, and low cost make it suitable as a matrix material in polymer composite matrix (PMC). PVA is hydrophilic, allowing for good interfacial adhesion properties and reinforcement with various filler materials (particles, fibers, flakes, nanoparticles, etc.) **(**Kuljanin *et al.* 2006**)**. PVA-based composites exhibit excellent mechanical properties and have diverse applications. However, PVA's complete solubility in water due to the presence of hydroxyl groups (OH-) limits its applicability, necessitating the study of its water solubility and water absorptivity (Jain *et al.* 2017). To reduce its hydrophilic nature, polyvinyl alcohol (PVA) is crosslinked with acids to engage its hydroxyl [OH^-] group, as PVA has high water absorptivity. As an alternative, it is used in combination with other polymers in multi-layered structures.

Carbonaceous materials have intrigued humans for centuries and are essential in organic chemistry and life due to their ability to combine with other elements. Carbon is found in nature as graphite or coal and as diamonds in smaller amounts. Man has created synthetic carbon forms for various applications, including composites for aircraft, electrical contacts, and gemstones. By incorporating graphite particles into the PVA matrix, stiffness, strength, and toughness can be improved. This reinforcement and resistance to deformation under stress are provided by the strong and stiff material. Controlling the amount and dispersion of graphite particles is crucial to achieving desired properties, excessive amounts result in brittleness, and inadequate amounts may not provide effective reinforcement. To use graphite in composite materials, its inert nature must be modified. This is done through oxidizing methods like gas or liquid exposure, plasma treatment, and electrochemical oxidation. Without surface modification, graphite cannot bond with other compounds, limiting its use as a reinforcement filler and hindering its ability to enhance mechanical properties.

2. Literature Review

Bio-polymer is increasingly being used as the primary material in the production of bio-composites due to its excellent physical strength, heat resistance, interface compatibility, and other properties. In the context of the impressive progress made in the development of biodegradable composites and their properties, this is particularly noteworthy. The purpose of this literature review is to provide a comprehensive examination of existing research on synthetic thermoplastic biodegradable polyvinyl alcohol (PVA), which is used as the matrix material for composite production. This section evaluates multiple studies on the mechanical and water absorption properties of PVA-based composites containing reinforcing particles or fibers at the nano/micro scale, as well as the diverse polymers used to produce PVA-based composite films. However, the propensity for high water uptake or solubility in water is a significant drawback of PVA-based composites/films. To overcome this limitation, researchers have explored cross-linking methods of PVA-based composites/films, which are also discussed in this review. Additionally, the review examines carbonaceous particles/fibers-reinforced composites, with a particular focus on their physical, mechanical, and thermal characteristics, particularly their mechanical properties.

2.1 Polyvinyl Alcohol (PVA) based reinforced composites

Over the past two decades, mechanical characteristics and water absorption rates of PVA-based reinforced films/composites were examined. The improved interfacial adhesion between the PVA matrix and fibers/particles resulted in more robust and resilient PVA composites, showing potential for diverse applications. The incorporation of reinforcing particles, fibers, and similar materials further enhanced the mechanical properties of PVA composites.

(Srinivasan et al. 2003) found that varying chitosan and PVA concentrations affected the mechanical properties of biocomposites. Chitosan-PVA (100-0) had the highest stiffness (1.874±0.342 GPa) and tensile strength (55.56±4.65 MPa), while Chitosan-PVA (0-100) had the highest ductility (105.47±6.8%). As chitosan decreased and PVA increased, elastic modulus and tensile strength decreased while elongation increased. (Sudhamani et al. 2003) investigated Gellan-PVA homopolymer films at varying ratios (3:1, 3:2, 1:1, 2:3, 1:3). Tensile strength of the composite biocomposites ranged from 3.5 to 5.6 MPa. As PVA increased, tensile strength decreased. (Kuljanin et al. 2006) produced a nanocomposite of lead sulphide (PbS) nanoparticles (NPs) (2.3 and 4.6 mass %) and polyvinyl alcohol (PVA) via colloidal chemistry. Tensile results demonstrated breaking strength increased up to 53.0±31 MPa with 4.6 mass% of PbS. (Roohani et al. 2008) developed a nanocomposite of Polyvinyl Alcohol, Polyvinyl Acetate, and cellulose whiskers (from cotton linter) as filler. Tensile tests showed improved properties with higher filler concentration but reduced properties with increased moisture content. (Yang et al. 2008) produced a slightly soluble nanofiber membrane via electro-spinning PVA cross-linked with maleic anhydride (MA) at varying ratios (PVA/MA = 30/1, 21/1, 20/1, 19/1, and 10/1). The fabricated membrane was boiled in water for 1 hour and PVA/MA (20/1) exhibited the lowest mass loss. (Lu et al. 2008) incorporated micro-fibrillated cellulose as reinforcement in a polyvinyl alcohol matrix to produce a composite film. The film was produced by blending a 5 wt. % PVA solution with water at 95°C for 2 h and adding MFC at varying weight percentages of 1%, 5%, 10%, and 15%. Mechanical testing showed that Young's modulus and tensile strength increased with increasing MFC content, reaching a maximum of 10 wt. % before stabilizing at higher MFC contents. At 10 wt. % MFC content, Young's modulus increased by 40%. (Shi et al. 2008) characterized a PVA/starch composite film cross-linked with citric acid. Tensile strength increased from 39 to 48 MPa when 5 wt. % citric acid was added. However, adding citric acid (from 5 to 30 wt. %) decreased tensile strength from 48 to 42 MPa and increased elongation at break from 102% to 208% due to plasticizing effect of residual citric acid. (Hyder et al. 2009) cross-linked chitosan-polyvinyl alcohol (CS-PVA) blend membranes and investigated their mechanical properties. Different ratios of CS-PVA (25-75, 50-50, 70-30, 75-25, and 80-20) were prepared using 5 wt. % PVA solution with DI water and 1 wt. % PVA solution with acetic acid. The blend membrane was then cross-linked using trimesoyl chloride (TMC)/hexane. The highest tensile strength of 74.5 ± 2.7 MPa was observed in the CS-PVA (80-20) blend. (Nath et al. 2010) reinforced a PVA matrix with fly ash (FA) modified with sodium lauryl sulphate (SLS) and compared it with an unmodified FA/PVA composite. The SLS-modified composite exhibited a 33% higher tensile strength than the unmodified composite. (Limpan et al. 2010) investigated bio-films made of FMP/PVA blends with varying ratios (10:0, 8:2, 6:4, 5:5, 4:6, 2:8, 0:10) and pH levels (3 and 11). The study revealed that a higher PVA percentage resulted in higher tensile strength, while a higher FMP percentage showed lower strength. Moreover, at pH level 3, higher PVA percentage films had higher strength, whereas, at pH level 11, higher FMP percentage films showed higher strength. (Ibrahim et al. 2010) created two composite films using PVA and nano-spherical cellulose from cotton linter and bleached linen. PVA/bleached linen film showed improved tensile strength and elongation at break up to 20 wt. %, whereas cotton linter composite had a continuous decrease in tensile strength. (Zhang et al. 2011) Produced PVA/cellulose fiber composite. Fibers were pan-milled to enhance dispersion and adhesion to PVA. Composite tensile strength improved with more pan-milling cycles. At 40 cycles, tensile strength increased to 16.4 MPa and elongation at break to 374%. (Qiu et al. 2012) created biodegradable PVA/MFC composite films with various compositions (5-50 wt. %). Composite crosslinking with glyoxal reduced swelling ability. Fracture strength increased from 34.1 MPa (pure PVA) to 89.9 MPa at 40 wt. % MFC. (Kannat et al. 2012) combined Chitosan (Ch) and PVA solutions with various ratios (1:1, 1:2 & 2:1), Glycerol (0.1% v/v) as a plasticizer, and ME or PE (0.1%) to fabricate films. Higher PVA concentration led to increased tensile strength. Incorporation of ME/PE increased tensile strength, with the highest value of 41.07±0.88 MPa seen in C1P2P (Ch: PVA ratio of 1:2 and 0.1% PE). (Xu et al. 2013) produced PVA cellulose nanocrystals (CNs) and silver nanoparticles (AgNPs) nanocomposite by solution casting with various CNs and AgNPs compositions. Tensile strength increased from 57.02 MPa (pure PVA) to a maximum of 81.21 MPa at a PVA/CNs/AgNPs ratio of 1.77. (Mandal and Chakrabarty 2014) generated sugarcane bagasse-derived nano-cellulose and PVA nano-composites with varying nano-cellulose percentages (2.5-10 wt. %). Crosslinking was done using 10 wt. % glyoxal. Unmodified PVA had 41.3 kPa tensile strength, whereas cross-linked PVA had 57.7 kPa. Addition of 7.5 wt. % nano-cellulose improved tensile strength by 48%. Cross-linked maximum strength was obtained with 5 wt. % nano-cellulose, resulting in a 44% increase over cross-linked PVA film. (Puyol et al. 2015) investigated the effect of trifluoroacetic acid (TFA) on PVA and PVA-cellulose composite. Young's modulus decreased from 2.75 GPa (pure PVA) to 25 MPa (PVA-TFA film) and elongation increased from 57% (pure PVA) to 693% (PVA-TFA film), indicating TFA acted as a plasticizer. (Ching et al. 2015) developed a PVA composite by incorporating cellulose nanocrystals and nano-silica as reinforcing agents. Films were made by stirring 10 wt. % PVA solution at 90°C for 2 hours, cooling it to room temperature, adding cellulose nanocrystals (1-7%) and 0.5% nano-silica. Increasing cellulose nanocrystals content increased Young's modulus from 15.45 MPa (pure PVA) to a maximum of 57.30 MPa at 15% cellulose nanocrystals**.** **(**Li et al. 2015) synthesized nanocomposite with PVA/cellulose nanowhiskers/chitosan and varied chitosan content. Low elongation at break observed with 15% chitosan added to 5% PVA and 1 wt.% CNWs. Enhanced tensile strength and elongation at break in PVA/CNWs composite due to hydrogen bonding between PVA chain and CNWs relative to neat PVA**.** **(**Ye et al. 2016) produced PVA composite films reinforced with eucalyptus lignosulfonate calcium (HLS) particles. Different weight ratios of HLS to PVA (0/100 to 60/40 wt. /wt.) were used. Pure PVA had a tensile strength of 48.4 MPa, Young's modulus of 707.9 MPa, and elongation at a break of 220.7%. Incorporating 35 wt. % of HLS significantly improved mechanical properties, increasing Young's modulus by 57.19% and tensile strength by 124.15%. (Sonker et al. 2016) developed a PVA-based crosslinked composite with glutaric acid modification and reinforced it with WSNTs. Three types of PVA films, neat PVA, TH-CL-PVA, and GA-CL-PVA, were prepared with WSNTs reinforcement. WSNT-TH-CL-PVA had the highest tensile strength at 139.9 MPa with Young's modulus of 7.1 GPa, while WSNT-GA-CL-PVA exhibited the highest toughness at 85.68 MPa. (Choo et al. 2016) blended chitosan (CS) and polyvinyl alcohol (PVA) with TEMPO-oxidized cellulose fiber (TOCN) to create bio-nanocomposite films. TOCNs were added at 0.5, 1.0, and 1.5 wt. %. PVA and CS showed hydrogen bonding interactions. TOCNs were uniformly distributed at lower filler concentrations but agglomerated at 1 wt. %. Tensile strength increased with reinforcement, but flexibility decreased at low loading. FTIR and XRD analyses indicated robust interaction between the polymer matrix and TCONs, leading to improved dispersion of the nanofillers. Thermal stability was slightly modified. (Jahan et al. 2016) assessed the KNO3 effect on CS-PVA (50-50) films. The 0.5g KNO3 film had 31.9 MPa tensile strength and 67% elongation at break. KNO3 ionic cross-linkage in blend films increased mechanical strength by 298.75% and elongation from 7.16% to 67%. (Kiro et al. 2017) created a Sericin-PVA composite with ZnO nanoparticles. Vickers hardness values were 15.11, 16.46, 17.39, 18.71, and 20.09 kg/mm2 by adding 200, 250, 300, and 350 mg of ZnO nanoparticles. (Marvdashti et al. 2017) studied AHSG/PVA composite film. Hydrogen bonds between polymers formed a homogeneous structure seen in FTIR & SEM. Increased PVA raised mechanical strength. But, an increase in AHSG reduced film ductility. (Tian et al. 2017) studied PVA/starch blend films' effect on composition and humidity. FTIR showed OH groups' hydrogen bonding between starch and PVA improved compatibility. Tensile strength, Young's modulus, and elongation at break decreased with increased starch content. But, 50% starch content remained flexible with elongation >1000% and tensile strength of 9 MPa, superior to LDPE films. (Sarwar et al. 2018) used nanocellulose and Ag nanoparticles to improve PVA nanocomposite films for antimicrobial food packaging. Mechanical and thermal properties improved; 5.23+0.27 MPa tensile strength increased to 12.32+0.61 MPa for 8 wt. % nanocellulose. The highest elongation at break was 518.10+0.25 at 12 wt. % nanocellulose. Ag nanoparticles further enhanced mechanical properties. Other properties examined include water vapor transmission rate and moisture retention capability. (Jain et al. 2019) reinforced basalt fiber in a PVA-based cross-linked composite. Reinforced film's UTS increased by 79.4% compared to cross-linked film. (Mahardika et al. 2021) reinforced PVA with Durian Peel Fibers cellulose for biocomposite films. 2%, 4%, 6%, and 8% reinforced fibers added. 6% cellulose fibers increased tensile strength by 54% compared to neat PVA but reduced elongation at break. Moisture resistance properties slightly improved due to the homogeneous dispersion of fibers in the PVA matrix. (Awad et al. 2021) investigated PVA/Hemp protein particles (HPP) composite and found that 12 wt. % HPP composites increased the tensile strength from 15.74 ± 0.72 MPa to 27.54 ± 0.45 MPa and Young's modulus from 282.51 ± 20.56 MPa to 988.69 ± 42.64 MPa. **Table 1** encapsulates the impact of reinforcement on the mechanical properties of PVA composites, presenting a concise and informative summary of the key findings.

Table 1. Effect of Reinforcement on Mechanical Properties of Polyvinyl Alcohol (PVA) Based Composites

Investigator & Year	Materials used	Sample preparation	Key findings

Srinivasan et al. (2003)	Chitosan-PVA biocomposites	Varying chitosan and PVA concentrations	Chitosan-PVA (100-0) had the highest stiffness (1.874±0.342 GPa) and tensile strength (55.56±4.65 MPa), while Chitosan-PVA (0-100) had the highest ductility (105.47±6.8%). As chitosan decreased and PVA increased, elastic modulus and tensile strength decreased while elongation increased.
Sudhamani et al. (2003)	Gellan-PVA homopolymer films	Varying ratios of 3:1, 3:2, 1:1, 2:3, 1:3	The tensile strength of the composite biocomposites ranged from 3.5 to 5.6 MPa. As PVA increased, tensile strength decreased.
Kuljanin et al. (2006)	PbS nanoparticles and PVA	Colloidal chemistry with lead sulphide (PbS) nanoparticles (NPs) (2.3 and 4.6 mass %)	Breaking strength increased up to 53.0±31 MPa with 4.6 mass% of PbS.
Roohani et al. (2008)	Polyvinyl Alcohol, Polyvinyl Acetate, and cellulose whiskers	Varying filler concentration	Tensile tests showed improved properties with higher filler concentration but reduced properties with increased moisture content.
Yang et al. (2008)	Electro-spun PVA cross-linked with maleic anhydride (MA)	Varying ratios of PVA/MA (30/1, 21/1, 20/1, 19/1, and 10/1)	PVA/MA (20/1) exhibited the lowest mass loss after boiling in water for 1 hour.
Lu et al. (2008)	Micro-fibrillated cellulose and PVA	Blending a 5 wt. % PVA solution with water at 95°C for 2 h and adding MFC at varying weight percentages of 1%, 5%, 10%, and 15%	Young's modulus and tensile strength increased with increasing MFC content, reaching a maximum of 10 wt. % before stabilizing at higher MFC contents. At 10 wt. % MFC content, Young's modulus increased by 40%.
Shi et al. (2008)	PVA/starch composite film cross-linked with citric acid	Varying concentrations of citric acid	Tensile strength increased from 39 to 48 MPa when 5 wt. % citric acid was added. However, adding citric acid (from 5 to 30 wt. %) decreased tensile strength from 48 to 42 MPa and increased elongation at break from 102% to 208% due to plasticizing effect of residual citric acid.
Hyder et al. (2009)	Chitosan-polyvinyl alcohol (CS-PVA) blend membranes	Different ratios of CS-PVA (25-75, 50-50, 70-30, 75-25, and 80-20)	The highest tensile strength of 74.5 ± 2.7 MPa was observed in the CS-PVA (80-20) blend after cross-linking using trimesoyl chloride
Nath et al. (2010)	PVA, fly ash (FA) modified with SLS	PVA matrix reinforced with fly ash modified with sodium lauryl sulphate (SLS) and compared with	SLS-modified composite exhibited a 33% higher tensile strength than the unmodified composite.

		an unmodified FA/PVA composite	
Limpan et al. (2010)	FMP/PVA blends with varying ratios	Bio-films made of FMP/PVA blends with varying ratios (10:0, 8:2, 6:4, 5:5, 4:6, 2:8, 0:10) and pH levels (3 and 11)	A higher PVA percentage resulted in higher tensile strength, while a higher FMP percentage showed lower strength. At pH level 3, higher PVA percentage films had higher strength, whereas, at pH level 11, higher FMP percentage films showed higher strength.
Ibrahim et al. (2010)	PVA and nano-spherical cellulose	Two composite films using PVA and nano spherical cellulose from cotton linter and bleached linen.	PVA/bleached linen film showed improved tensile strength and elongation at break up to 20 wt. %, whereas cotton linter composite had a continuous decrease in tensile strength.
Zhang et al. (2011)	PVA/cellulose fiber composite	PVA/cellulose fiber composite. Fibers were pan-milled to enhance dispersion and adhesion to PVA.	Composite tensile strength improved with more pan-milling cycles. At 40 cycles, tensile strength increased to 16.4 MPa and elongation at break to 374%.
Qiu et al. (2012)	PVA/MFC composite films	Biodegradable PVA/MFC composite films with various compositions (5-50 wt. %). Composite crosslinking with glyoxal reduced swelling ability.	Fracture strength increased from 34.1 MPa (pure PVA) to 89.9 MPa at 40 wt. % MFC.
Kannat et al. (2012)	PVA and Chitosan (Ch)	Chitosan (Ch) and PVA solutions with various ratios (1:1, 1:2 & 2:1), Glycerol (0.1% v/v) as a plasticizer, and ME or PE (0.1%) to fabricate films.	Higher PVA concentration led to increased tensile strength. Incorporation of ME/PE increased tensile strength, with the highest value of 41.07±0.88 MPa seen in C1P2P (Ch: PVA ratio of 1:2 and 0.1% PE).
Xu et al. (2013)	PVA cellulose nanocrystals (CNs)	PVA cellulose nanocrystals (CNs) and silver nanoparticles (AgNPs) nanocomposite by solution casting with various CNs and AgNPs compositions.	Tensile strength increased from 57.02 MPa (pure PVA) to a maximum of 81.21 MPa at a PVA/CNs/AgNPs
Mandal and Chakrabarty (2014)	PVA/nano-cellulose	Varying nano-cellulose percentages (2.5-10 wt. %). Crosslinking was done using 10 wt. % glyoxal.	Addition of 7.5 wt. % nano-cellulose resulted in roughly 48% improvement in tensile strength. Cross-linking with glyoxal increased strength up to 44% with 5 wt. % of nano-cellulose content.

Puyol et al. (2015)	PVA, PVA-cellulose composite, trifluoroacetic acid (TFA)	Films were made by adding TFA to PVA and PVA-cellulose composite	Young's modulus decreased from 2.75 GPa (pure PVA) to 25 MPa (PVA-TFA film) and elongation increased from 57% (pure PVA) to 693% (PVA-TFA film), indicating TFA acted as a plasticizer.
Ching et al. (2015)	PVA, cellulose nanocrystals, nano-silica	Films were made by stirring 10 wt. % PVA solution at 90°C for 2 hours, cooling it to room temperature, adding cellulose nanocrystals (1-7%) and 0.5% nano-silica	Increasing cellulose nanocrystals content increased Young's modulus from 15.45 MPa (pure PVA) to a maximum of 57.30 MPa at 15% cellulose nanocrystals.
Li et al. (2015)	PVA, cellulose nanowhiskers, chitosan	Nanocomposite was prepared by adding chitosan to PVA and CNWs	Low break elongation with 15% chitosan, 5% PVA, and 1 wt.% CNWs. PVA/CNWs composite showed increased tensile strength and elongation at break due to hydrogen bonding with CNWs compared to neat PVA.
Ye et al. (2015)	PVA, eucalyptus lignosulfonate calcium (HLS)	Different weight ratios of HLS to PVA (0/100 to 60/40 wt. /wt.) were used	Incorporating 35 wt. % of HLS significantly improved mechanical properties, increasing Young's modulus by 57.19% and tensile strength by 124.15%. Pure PVA had a tensile strength of 48.4 MPa, Young's modulus of 707.9 MPa, and elongation at a break of 220.7%.
Sonker et al. (2016)	PVA, glutaric acid, WSNTs	Three types of PVA films, neat PVA, TH-CL-PVA, and GA-CL-PVA, were prepared with WSNTs reinforcement	WSNT-TH-CL-PVA had the highest tensile strength at 139.9 MPa with Young's modulus of 7.1 GPa, while WSNT-GA-CL-PVA exhibited the highest toughness at 85.68 MPa.
Choo et al. (2016)	PVA, chitosan (CS), TEMPO-oxidized cellulose fiber (TOCN)	Blended chitosan (CS) and polyvinyl alcohol (PVA) with TOCN to create bio-nanocomposite films	Tensile strength increased with reinforcement, but flexibility decreased at low loading. FTIR and XRD analyses indicated robust interaction between the polymer matrix and TCONs, leading to improved dispersion of the nanofillers. Thermal stability was slightly modified.
Jahan et al. (2016)	CS-PVA (50-50) blend films, KNO3	KNO3 was added to the blend films	The 0.5g KNO3 film had 31.9 MPa tensile strength
Kiro et al. (2017)	PVA, and ZnO nanoparticles	Varying % of ZnO nanoparticles	Vickers hardness values were 15.11, 16.46, 17.39, 18.71, and 20.09 kg/mm2 by adding 200, 250, 300, and 350 mg of ZnO nanoparticles

Marvdashti et al. (2017)	AHSG/PVA composite film	Hydrogen bonds between polymers formed a homogeneous structure seen in FTIR & SEM	Increased PVA raised mechanical strength. But, an increase in AHSG reduced film ductility.
Tian et al. (2017)	PVA/starch blend films	Different % of starch in PVA mixed	Tensile strength, Young's modulus, and elongation at break decreased with increased starch content. But, 50% starch content remained flexible with elongation >1000% and tensile strength of 9 MPa, superior to LDPE films.
Sarwar et al. (2018)	PVA nanocomposite films with nanocellulose and Ag nanoparticles	Varying % of nanocellulose and Ag nanoparticles in PVA	5.23+0.27 MPa tensile strength increased to 12.32+0.61 MPa for 8 wt. % nanocellulose. The highest elongation at break was 518.10+0.25 at 12 wt. % nanocellulose. Ag nanoparticles further enhanced mechanical properties.
Jain et al. (2019)	Basalt fiber in PVA-based cross-linked composite	Varying % of Basalt fibers	Reinforced film's UTS increased by 79.4% compared to cross-linked film
Mahardika et al. (2021)	PVA reinforced with Durian Peel Fibers cellulose for biocomposite films	2%, 4%, 6%, and 8% reinforced fibers added	6% cellulose fibers increased tensile strength by 54% compared to neat PVA but reduced elongation at break. Moisture resistance properties slightly improved due to the homogeneous dispersion of fibers in the PVA matrix.
Awad et al. (2021)	PVA/Hemp protein particles (HPP) composite	Varying % of HPP	12 wt. % HPP composite increased the tensile strength from 15.74 ± 0.72 MPa to 27.54 ± 0.45 MPa and Young's modulus from 282.51 ± 20.56 MPa to 988.69 ± 42.64 MPa.

2.2 Water absorption properties of PVA-based cross-linked/composite films

PVA's water absorption/swelling and water-soluble nature is a major drawback due to its hydroxyl (–OH) group. This hydrophilic nature leads to a decrease in mechanical strength. However, engaging its hydroxyl (–OH) group with acidic treatment or filler material overcomes this disadvantage, called acidic cross-linking. In hot food packaging, PVA-based composite films are advantageous due to their high vapor permeability. Researchers have attempted to reduce the hydrophilic nature of PVA-based composite films through various treatments.

(Srinivasa et al. 2003) found that polyvinyl alcohol blend film's water solubility decreases with an increase in chitosan percentage, while pure PVA is soluble in water. Higher pH values result in higher solubility. (Helen et al. 2006) developed a hybrid membrane by combining zirconium phosphate, hetero-polyacid cesium salt, and PVA. An aqueous solution of 10 wt. % PVA, 30 wt. % orthophosphoric acid, and 10 wt. % zirconium phosphate was used to produce the membrane. Water absorption tests were conducted after immersing the film in deionized water for 2 hours. The PVA-ZrP-Cs1-SWA hybrid membrane had 240% water uptake, while the PVA-ZrP-Cs2-SWA hybrid membrane had 140% water uptake. Crosslinking with 0.5 wt. /vol. % TMC/hexane reduced the PVA swelling degree from 68-72%. The swelling power of the composite film decreased from 105% (neat PVA) to 78.3% (cross-linked PVA) when cross-linked with glyoxal. (Shi et al. 2008) investigated PVA/starch film with citric acid crosslinking. Citric acid was used at 5 – 30 wt. %. The film's water absorbance decreased from 33 % to 20 % with increasing citric acid percentage. (Figueiredo et al. 2009) evaluated mild conditions for PVA crosslinked films, enhancing water resistance without organic solvents or acid catalysts. Glutaraldehyde was used due to its intermolecular reaction and non-selective protein binding. A 2.7-fold decrease in oxygen permeability demonstrated effective crosslinking. The optimal GA/PVA mass ratio for the highest crosslinking density was 0.01, whereas more GA resulted in branching and increased water solubility due to lost packing capacity. (Zhou et al. 2009) utilized UV irradiation to prepare and characterize surface crosslinked thermoplastic starch/PVA. The blend films were soaked in an aqueous sodium benzoate solution. The most effective surface photo crosslinking occurred at 0.75% for 30 seconds. Surface photo crosslinking reduced surface hydrophilicity and increased water resistance, along with an increase in tensile strength and Young's modulus and a decrease in elongation at break. (Wang et al. 2010) investigated crosslinking of PVA fibrous membranes using PEG Diacylchloride and Glutaraldehyde. Crosslinking with GA and PEG Diacylchloride produced a hydrophilic and water-stable PVA fibrous membrane. GA/ethanol crosslinking increased crystalline structure, whereas GA/NasSO4 reduced it. Complete loss of crystalline structure was observed with PEG diacyl chloride crosslinking in toluene/pyridine. A hydrophobic PVA fibrous membrane with minimal change in the interfiber porous structure was formed by using lower and shorter PEG extents. (Abdulkhani et al. 2013) compared the water uptake of cellulose and cellulose/PVA film. The presence of the hydroxyl group resulted in higher water uptake for cellulose/PVA film, ranging from 73% to 78%, as compared to cellulose film at 33% to 42%. (Stone et al. 2013) demonstrated citric acid as a crosslinker for PVA/alginate nanofibers. 5% citric acid in electrospinning produced a porous nanofiber network with random orientation. Crosslinked fibers were more stable and insoluble in water/simulated body fluid, unlike non-crosslinked ones. (Wang et al. 2014**)** cross-linked xylan/polyvinyl alcohol composite films with citric acid and examined the effects of citric acid content and PVA/xylan ratio on mechanical properties, thermal stability, solubility, degree of swelling, and water vapor permeability. Moisture permeability was influenced by citric acid content but not by PVA/xylan ratio. Citric acid improved the interactions between PVA and xylan by promoting hydrogen and ester bond formation. Notably, the degree of swelling and moisture permeability were significantly affected by the citric acid content in the film formulations. (Sonker et al. 2016) cross-linked PVA films using glutaric acid at 125 ºC for 0.5-12 h, resulting in TH-CL-PVA and GA-CL-PVA films with 69.7% and 24.9% swelling, respectively, compared to 152.8% swelling for PVA alone. (Marvdashti et al. 2017) compared the solubility of PVA and PVA/AHSG (Alyssum homolocarpum seed gum) film. The solubility of AHSG film decreased as the percentage of AHSG increased, with a solubility of 13±1.3%. PVA had a much higher solubility of 75±3.5%. (Tian et al. 2017) studied how starch content affected water uptake in PVA/starch blend film. Increased starch content reduced the degree of crystallinity and water uptake at equilibrium, while water uptake at equilibrium increased with higher RH. (Asem et al. 2018) optimized water absorption in PVA-starch biocomposites reinforced with sugarcane bagasse nanofibers using a two-level factorial design. The combination of PVA (1g) + nanocellulose (1g) + starch (1g) in 80 ml water showed the lowest water absorption of 64.7%. (Jain et al. 2019) reinforced HCl-crosslinked PVA-based film with basalt fiber and found that water absorption decreased with increasing basalt fiber content. The crosslinked film initially absorbed 128.6% water due to C-Cl bond formation. The findings presented in **Table 2** demonstrate that both reinforcement and crosslinking have a notable impact on the water uptake of PVA-based composite films. The specific types of reinforcement and the degree of crosslinking were found to be critical factors in determining the water absorption behaviour of the films.

Table 2. Water Absorption Properties of PVA-Based Cross-linked/Composite Films

Investigator & Year	Materials Used	Sample Preparation	Key Findings
Srinivasa et al. (2003)	PVA blend film, chitosan	Varying chitosan percentage	Water solubility decreases with an increase in chitosan percentage; pure PVA is soluble in water; higher pH values result in higher solubility
Helen et al. (2006)	PVA, zirconium phosphate, hetero-polyacid cesium salt	An aqueous solution of PVA, orthophosphoric acid, and zirconium phosphate	PVA-ZrP-Cs1-SWA hybrid membrane had 240% water uptake, while the PVA-ZrP-Cs2-SWA hybrid membrane had 140% water uptake; crosslinking with 0.5 wt. /vol. % TMC/hexane reduced the PVA swelling degree from 68-72%; the swelling power of the composite film decreased from 105% (neat PVA) to 78.3% (cross-linked PVA) when cross-linked with glyoxal
Shi et al. (2008)	PVA/starch film, citric acid	Varying citric acid percentage	Water absorbance decreased from 33 % to 20 % with increasing citric acid percentage
Figueiredo et al. (2009)	PVA film, glutaraldehyde	Varying GA/PVA mass ratio	A 2.7-fold decrease in oxygen permeability demonstrated effective crosslinking; the optimal GA/PVA mass ratio for the highest crosslinking density was 0.01
Zhou et al. (2009)	Thermoplastic starch/PVA blend film	Soaked in aqueous sodium benzoate solution	Surface photo crosslinking at 0.75% for 30 seconds reduced surface hydrophilicity and increased water resistance, along with an increase in tensile strength and Young's modulus and a decrease in elongation at break
Wang et al. (2010)	PVA fibrous membrane, PEG Diacylchloride, glutaraldehyde	Varying crosslinking agents and conditions	GA and PEG Diacylchloride crosslinking developed a hydrophilic and water-stable PVA fibrous membrane; lower and shorter PEG extents created a hydrophobic PVA fibrous membrane with minimal change in the interfiber porous structure
Abdulkhani et al. (2013)	Cellulose/PVA film, cellulose film	Varying cellulose and PVA ratio	Cellulose/PVA film had higher water uptake ranging from 73% to 78%, as

			compared to cellulose film at 33% to 42% due to the presence of the hydroxyl group.
Stone et al. (2013)	PVA/alginate nanofibers, citric acid	Electrospinning with 5% citric acid	Crosslinked fibers were more stable and insoluble in water/simulated body fluid, unlike non-crosslinked ones
Wang et al. (2014)	Xylan/PVA composite films, citric acid	Varying citric acid content and PVA/xylan ratio	Moisture permeability was affected by citric acid content, not by PVA/xylan ratio; citric acid strengthened the interactions between PVA and xylan, leading to hydrogen and ester bond formation
Sonker et al. (2016)	PVA films and glutaric acid	Cross-linking with glutaric acid	TH-CL-PVA and GA-CL-PVA films had 69.7% and 24.9% swelling, respectively, compared to 152.8% swelling for PVA alone.
Marvdashti et al. (2017)	PVA and PVA/AHSG film	Solubility comparison	AHSG film solubility decreased as the percentage of AHSG increased (13±1.3%). PVA had much higher solubility (75±3.5%).
Tian et al. (2017)	PVA/starch blend film	Study of water uptake with a varying starch content	Increased starch content reduced the degree of crystallinity and water uptake at equilibrium. Water uptake at equilibrium increased with higher relative humidity (RH).
Asem et al. (2018)	PVA-starch biocomposites reinforced with sugarcane bagasse nanofibers	Two-level factorial design optimization	The combination of PVA (1g) + nanocellulose (1g) + starch (1g) in 80 ml water showed the lowest water absorption of 64.7%.
Jain et al. (2019)	HCl-crosslinked PVA-based film with basalt fiber	Reinforcement with basalt fiber	Water absorption decreased with increasing basalt fiber content. The crosslinked film initially absorbed 128.6% water due to C-Cl bond formation.

2.3 Carbonaceous materials as reinforcement material in PVA matrix

(Liu et al. 2009) created graphite/PVA hydrogel composites for an artificial cornea using particle leaching and thawing. FT-IR and XRD showed chemical interaction between PVA and graphite. PVA/graphite hydrogel had milder inflammation and increased cell infiltration, migration, neovascularization, and tissue growth than PVA hydrogel alone. The porous PVA/graphite hydrogel had sufficient mechanical strength and high porosity. (Liang et al. 2009) fabricated graphene oxide (GO) reinforced polyvinyl alcohol (PVA) nanocomposites using the solution casting method and evaluated the dispersion of individual graphite oxides. The addition of 0.7 wt. % GO increased Young's modulus and tensile strength by 62% (from 2.13 to 3.45 GPa) and 76% (from 49.9 to 87.6 MPa), respectively. Moreover, graphene/PVA nanocomposites displayed enhanced thermal stability. (Naseh et al. 2009) utilized nitric acid oxidation and DBD plasma to modify CVD-produced carbon nanotubes. After purification, FT-IR analysis showed the emergence of C=O and COOH groups. Nitric acid treatment was more aggressive and created more functional groups, while plasma treatment only altered the surface. Chemical treatment affected the bulk of the material. (Aviles et al. 2009) examined carbon nanotube purification and functionalization with nitric and sulphuric acid, plus hydrogen peroxide. Low acid concentrations, brief treatment times, and low sonication power were used. FT-IR analysis showed an increase in OH and C=O groups. 3M HNO3 treatment for 2 hours was more successful than 8M treatment in functionalizing the nanotube surfaces. (Zhao et al. 2010) produced uniform and well-dispersed PVA-graphene composite films via the incorporation of graphene oxide, then reduced to graphene nanosheets. 1.8% graphene volume increases enhanced tensile strength by 150%, with effective load transfer between the matrix and graphene. The composite's modulus was ten times higher than pure PVA with 1.8% graphene. (Dongil et al. 2010) investigated surface chemical changes from functionalization and oxidation on HSAG and CNFs. Aqueous HNO3 wet oxidation and oxygen plasma oxidation were used. CNFs were more affected by plasma therapy. Wet oxidation raised group numbers on HSAG, but not on graphitized CNFs. (Cano et al. 2013) esterified GO's carboxylic groups with PVA's hydroxyl groups to covalently functionalize GO into f-(PVA) GO. Functionalized graphene oxide was used to form paper-like material by vacuum filtration. f-(PVA) GO paper's mechanical properties were superior to those of GO and PVA mixtures. f-(PVA) GO composites had about 60% higher modulus and strength at a loading below 0.3 vol.%. (Li et al. 2013) examined the effect of ultrasonication on a GO-PVA composite's mechanical properties. GO was ultrasonicated for up to 5 hours before being mixed with 10 wt.% PVA DI water solution. The composite had a tensile strength of 12.6% higher than the pristine PVA film. Ultrasonication for 30 minutes produced a maximum strength of 82.5 MPa. (Chen et al. 2015) utilized an aqueous solution method to produce a boric acid crosslinked polyvinyl alcohol (PVA) composite with graphene oxide (GO). Addition of 0.2 wt. % GO and 5 wt. % boric acid increased tensile strength from 23.3 to 53.4 MPa and 67.7 MPa, respectively. The combination of 0.2 wt.% GO and 5 wt.% boric acid resulted in further enhancement of tensile strength to 85.5 MPa, proving the composite's improved mechanical and thermal properties. (Dalmis et al. 2016) studied the impact of nanoparticulate reinforcement on ZA27 alloy composites with nano-sized graphite particles. Physical and mechanical properties, including density, hardness, and tensile strength, were measured, and microstructure was analyzed using SEM. The findings revealed that higher graphite content led to increased porosity and decreased density in the nanocomposites. Additionally, ultimate tensile strength (UTS) and Brinell hardness values also decreased with increasing graphite content. (Anstey et al. 2016) modified Miscanthus-derived Biocarbon with oxidative acidic treatment using nitric acid, sulphuric acid, and their mixture. Refluxing with 70% HNO3 and 95% H2SO4 for 6 hours led to the addition of carboxylic acid and nitro groups, as confirmed by FT-IR spectra. H2SO4 treatment caused a slight increase in sulphur and oxygen content. The HNO3-H2SO4 treatment was found to be the most effective, improving functionality for better polymer matrix interaction. (Kashyap et al. 2016) prepared PVA nanocomposites by reinforcing graphene oxide (GO). PVA/GO (0.3 wt. %) showed a 150% increase in tensile strength compared to neat PVA. Neat PVA film had a tensile strength of 25.3±3 MPa, whereas PVA-GO had a tensile strength of 63±5 MPa. Additionally, PVA-GO had Young's modulus of 5.82±0.6 MPa, while PVA film had Young's modulus of 2.32±0.3 MPa. (Jose et al. 2017) used citric acid as a crosslinking agent and glycerol as a plasticizer to prepare polyvinyl alcohol/starch/graphene nanocomposites. Crosslinking improved interaction between PVA and/or starch hydroxyl groups and graphene sheet oxygen-containing groups. The addition of graphene increased modulus and tensile strength, from 24.2 to 53.3 MPa and 6.7 to 10 MPa, respectively, while elongation-at-break rose from 27.5 to 57.2%. The optimal matrix contained 0.5 wt% of graphene. However, the addition of starch decreased tensile strength. (Sezer et al. 2019) investigated the reflux of Multiwalled carbon nanotubes with varying molar concentrations of HNO3 and HNO3/H2SO4. The 15M HNO3 treatment produced MWCNTs with the highest oxygen content of 5.15%. The weight loss was 17%, 6.8%, and 5% for 10M H2SO4/HNO3, 15M HNO3, and 10M HNO3, respectively. The 15M HNO3-treated MWCNTs exhibited the highest dispersion stability. (Hammood et al. 2019) used powder metallurgy to prepare graphite particles in Nickel - 5 vol. % Zirconium dioxide composites with 0, 2, 4, 6, and 8 vol. %. After mixing the powders, the samples were pressed at 900 MPa for one minute and sintered for three hours at 1160˚C. Hybrid composites with 4% graphite particles displayed high mechanical and wear properties. Increasing graphite content resulted in a decrease in bulk and apparent densities, but an increase in total porosity, apparent porosity, and water absorption. Diametral compressive strength, microhardness, and wear resistance increased by up to 4% with the addition of graphite particles. However, at higher applied loads, all reinforcement content showed decreased wear resistance. (Irhayyim et al. 2020) tested aluminium and graphite self-lubricating composites with varying MgO nanoparticle percentages. XRD and SEM were used for characterization, and dry sliding wear tests were conducted. MgO nanoparticles improved micro-hardness and diametral compressive strength up to 2.5 wt. percent, but further increase caused a decrease. The wear rate was lower than without MgO for 1.5 or 3.5 wt. percent, and increased at 2.5 wt. percent for all loads. The composite with 2.5 wt. percent MgO had the best wear and mechanical properties. (Singh et al. 2020) studied functionalized graphite particles as reinforcement in PVA composites. Neat PVA was compared with 1 wt. % functionalized graphite particles, which resulted in 62.5% higher ultimate tensile strength. The highest damping coefficient of 0.573 was found in cross-linked PVA. The effect of weight percentage of functionalized graphite particles, ranging from 0 to 2 wt. %, on physical, mechanical, and thermal properties was analyzed. **Table 3** summarizes the improvements in the mechanical properties of PVA matrix composites achieved by incorporating carbonaceous reinforcements, such as graphite nanoparticles, carbon nanotubes, fibers, and graphene, and their surface modifications. The data shows significant enhancements in tensile strength, flexural strength, impact strength, elastic modulus, and thermal conductivity.

Table 3. Impact of Carbonaceous Reinforcements on Mechanical Properties of PVA Matrix

Investigator & Year	Materials Used	Procedural specification	Key Findings
Liu et al. (2009)	Graphite/PVA hydrogel composites	Particle leaching and thawing	Chemical interaction between PVA and graphite is shown via FT-IR and XRD. PVA/graphite hydrogel had milder inflammation and increased cell infiltration, migration, neovascularization, and tissue growth than PVA hydrogel alone. Porous PVA/graphite hydrogel had sufficient mechanical strength and high porosity.
Liang et al. (2009)	Polyvinyl alcohol (PVA) nanocomposites reinforced with graphene oxide (GO)	Solution casting method	With 0.7 wt. % of GO, Young's modulus, and tensile strength increased by 62% (from 2.13 to 3.45 GPa) and 76% (from 49.9 to 87.6 MPa), respectively. Graphene/PVA nanocomposites also exhibited improved thermal stability.

Naseh et al. (2009)	CVD-produced carbon nanotubes	Nitric acid oxidation and DBD plasma	FT-IR analysis showed the emergence of C=O and COOH groups after purification. The nitric acid treatment created more functional groups, while the plasma treatment only altered the surface. Chemical treatment affected the bulk of the material.
Aviles et al. (2009)	Carbon nanotubes	Nitric and sulphuric acid, hydrogen peroxide	FT-IR analysis showed an increase in OH and C=O groups. 3M HNO3 treatment for 2 hours was more successful than the 8M treatment in functionalizing the nanotube surfaces.
Zhao et al. (2010)	PVA-graphene composite films	Incorporation of graphene oxide, then reduced to graphene nanosheets	1.8% graphene volume increase enhanced tensile strength by 150%. The composite's modulus was ten times higher than pure PVA with 1.8% graphene.
Dongil et al. (2010)	HSAG and CNFs	Aqueous HNO3 wet oxidation and oxygen plasma oxidation	CNFs were more affected by plasma therapy. Wet oxidation raised group numbers on HSAG, but not on graphitized CNFs.
Cano et al. (2013)	Graphene oxide (GO)	Esterification with PVA's hydroxyl groups to covalently functionalize GO	Functionalized graphene oxide (f-(PVA) GO) was used to form paper-like material by vacuum filtration. f-(PVA) GO paper's mechanical properties were superior to those of GO and PVA mixtures. f-(PVA)GO composites had about 60% higher modulus and strength at a loading below 0.3 vol.%.
Li et al. (2013)	Graphene oxide (GO), PVA DI water solution	GO ultrasonicated for up to 5 hours before being mixed with 10 wt.% PVA DI water solution	The tensile strength of the composite was 12.6% higher than pristine PVA film. Ultrasonication for 30 minutes produced maximum strength of 82.5 MPa.
Chen et al. (2015)	Graphene oxide (GO), boric acid, polyvinyl alcohol (PVA)	Aqueous solution method used to produce boric acid crosslinked PVA composite with GO.	Addition of 0.2 wt. % GO and 5 wt. % boric acid increased tensile strength to 53.4 MPa and 67.7 MPa, respectively. Combination of 0.2 wt. % GO and 5 wt. % boric acid resulted in further enhancement of tensile strength to 85.5 MPa.
Dalmis et al. (2016)	ZA27 alloy, nano-sized graphite particles	Nanoparticulate reinforcement added to ZA27 alloy composites	The porosity ratio increased and density values decreased as graphite content increased. Ultimate tensile strength (UTS) and Brinell hardness values decreased as well with an increase in graphite content.

Anstey et al. (2016)	Miscanthus-derived Biocarbon	Biocarbon modified with oxidative acidic treatment using nitric acid, sulphuric acid, and their mixture	Refluxing with 70% HNO_3 and 95% H_2SO_4 for 6 hours led to the addition of carboxylic acid and nitro groups. HNO_3-$H2SO_4$ treatment was the most effective, improving functionality for better polymer matrix interaction.
Kashyap et al. (2016)	Graphene oxide (GO), polyvinyl alcohol (PVA)	PVA nanocomposites reinforced with GO	PVA/GO (0.3 wt. %) showed a 150% increase in tensile strength compared to neat PVA. PVA-GO had Young's modulus of 5.82±0.6 MPa, while PVA film had Young's modulus of 2.32±0.3 MPa.
Jose et al. (2017)	Polyvinyl alcohol (PVA), starch, graphene	PVA/starch/graphene nanocomposites prepared using citric acid as a crosslinking agent and glycerol as a plasticizer	The addition of graphene increased modulus and tensile strength, from 24.2 to 53.3 MPa and 6.7 to 10 MPa, respectively, while elongation-at-break rose from 27.5 to 57.2%. The optimal matrix contained 0.5 wt. % of graphene.
Sezer et al. (2019)	Multiwalled carbon nanotubes, HNO_3, H_2SO_4	Reflux of MWCNTs with varying molar concentrations of HNO_3 and HNO_3/H_2SO_4	The 15M HNO_3 treatment produced MWCNTs with the highest oxygen content of 5.15%. Weight loss was 17%, 6.8%, and 5% for 10M H_2SO_4/HNO_3, 15M HNO_3, and 10M HNO_3, respectively. The 15M HNO_3-treated MWCNTs exhibited the highest dispersion stability.
Hammood et al. (2019)	Graphite particles, Nickel, Zirconium dioxide	Powder metallurgy with 0, 2, 4, 6, and 8 vol. % graphite particles	Hybrid composites with 4% graphite particles displayed high mechanical and wear properties. Increasing graphite content resulted in a decrease in bulk and apparent densities, but an increase in total porosity, apparent porosity, and water absorption. Diametral compressive strength, microhardness, and wear resistance increased by up to 4% with the addition of graphite particles. However, at higher applied loads, all reinforcement content showed decreased wear resistance.
Irhayyim et al. (2020)	Aluminum, graphite, and MgO nanoparticles	Varying MgO nanoparticle percentages	MgO nanoparticles improved micro-hardness and diametral compressive strength up to 2.5 wt. percent but further increase caused a decrease. The wear rate was lower than without MgO for 1.5 or 3.5 wt. percent and increased at 2.5 wt. percent for all loads. The

			composite with 2.5 wt. percent MgO had the best wear and mechanical properties.
Singh et al. (2020)	Functionalized graphite particles, PVA	Neat PVA and PVA with 1 wt. % functionalized graphite particles, varying weight percentages of functionalized graphite particles	PVA with 1 wt. % functionalized graphite particles had 62.5% higher ultimate tensile strength. The highest damping coefficient of 0.573 was found in cross-linked PVA. The effect of the weight percentage of functionalized graphite particles on physical, mechanical, and thermal properties was analyzed.

Conclusion

1. Polyvinyl alcohol (PVA) is a versatile and highly sought-after thermoplastic polymer due to its biocompatible, non-toxic, and biodegradable properties.
2. PVA exhibits exceptional mechanical and thermal properties, making it highly suitable for diverse applications across multiple fields.
3. Despite its advantages, PVA's hydrophilicity remains a significant disadvantage that researchers have attempted to address through the use of filler materials or cross-linking in PVA-based composites.
4. Several studies have investigated the water absorption and mechanical behavior of PVA composites and highlighted the crucial role of filler materials in enhancing interfacial adhesion properties.
5. In-depth research has been conducted to analyze the impact of incorporating different types of filler materials like particles, nanoparticles, fibers, and flakes on the properties of PVA composites.
6. Carbonaceous materials, with their low energy state and layered crystal structure, are highly beneficial in a wide range of applications.
7. The absence of reactive ion groups in carbonaceous materials, such as graphite, limits their interaction with monomers, but surface modifications like oxidation, chemical functionalization, or physical treatments have enabled intercalation and other chemical reactions. These modifications have demonstrated an improvement in the mechanical properties of polymer matrix composites (PMCs) by enhancing interfacial adhesion.
8. Researchers have explored various techniques to modify carbonaceous materials like graphite particles to improve their interfacial adhesion properties with polymer matrices, such as high-energy milling or plasma treatment.
9. These studies provide valuable insight into the potential applications of PVA and carbonaceous material-based composites, and they also offer guidance on optimizing their properties through filler material selection and surface modifications.

10. PVA and its composites are promising for 3D printing due to their flowability, stimuli-responsivity, biocompatibility, biodegradability, and mechanical/chemical strength, making them attractive for diverse applications.

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

Abdulkhani A., Hojati Marvast E., Ashori A., Hamzeh Y., and Karimi, A. N. (2013). Preparation of cellulose/polyvinyl alcohol biocomposite films using 1-n-butyl-3-methylimidazolium chloride. Int. J. Biol. Macromol., 62, 379–386.

Anstey A., Vivekanandhan S., Rodriguez-Uribe A., Misra M., Mohanty A. K. (2016). Oxidative Acid Treatment and Characterization of New Biocarbon from Sustainable Miscanthus Biomass. *Sci. Total Environ.,* 550, 241–247.

Asem M., Nawawi W. M. F. W., and Jimat D. N. (2018). Evaluation of water absorption of polyvinyl alcohol-starch biocomposite reinforced with sugarcane bagasse nanofibre: Optimization using Two-Level Factorial Design. *IOP Conf. Ser.: Mater. Sci*. Eng., 368, 012005.

Aviles F., Cauich-Rodríguez J. V., Moo-Tah L., May-Pat A., Vargas-Coronado R. (2009). Evaluation of Mild Acid Oxidation Treatments for MWCNT Functionalization. *Carbon*, 47, 2970–2975.

Awad S. A. (2021). Enhancing the Thermal and Mechanical Characteristics of Polyvinyl Alcohol (PVA)-Hemp Protein Particles (HPP) Composites. *Int. Polym. Process,* 36(2), 137-143.

Cano M., Khan U., Sainsbury T., O'Neill A., Wang Z., McGovern I. T., Maser W. K., Benito A. M., Coleman J. N. (2013). Improving the Mechanical Properties of Graphene Oxide Based Materials by Covalent Attachment of Polymer Chains. *Carbon*, 52, 363–371.

Chen J., Li Y., Zhang Y., Zhu Y. (2015). Preparation and Characterization of Graphene Oxide Reinforced PVA Film with Boric Acid as Crosslinker. *J. Appl. Polym. Sci.*, 132, n/a-n/a.

Ching Y. C., Rahman A., Ching K. Y., Sukiman N. L., Cheng H. C. (2015). Preparation and Characterization of Polyvinyl Alcohol-Based Composite Reinforced with Nanocellulose and Nanosilica. *Bio Resources*, 10(2), 3364-3377.

Choo K., Ching Y., Chuah C., Julai S., Liou N.-S. (2016). Preparation and Characterization of Polyvinyl Alcohol-Chitosan Composite Films Reinforced with Cellulose Nanofiber. *Materials*, 9, 644.

Dalmis R., Cuvalci H., Canakci A., and Guler O. (2016). Investigation of Graphite Nano Particle Addition on the Physical and Mechanical Properties of ZA27 Composites. *Adv. Compos. Lett.,* 25(2), 096369351602500.

Dongil A. B., Bachiller-Baeza B., Guerrero-Ruiz A., Rodríguez-Ramos I., Martínez-Alonso A., and Tascón J. M. D. (2011). Surface chemical modifications induced on high surface area graphite and carbon nanofibers using different oxidation and functionalization treatments. *J. Colloid Interface Sci.,* 355(1), 179–189.

Figueiredo K. C. S., Alves T. L. M., Borges C. P. (2009). Poly (Vinyl Alcohol) Films Crosslinked by Glutaraldehyde under Mild Conditions. *J. Appl. Polym. Sci.*, 111, 3074–3080.

Guzman-Puyol S., Ceseracciu L., Heredia-Guerrero J. A., Anyfantis G. C., Cingolani R., Athanassiou A., and Bayer I. S. (2015). Effect of trifluoroacetic acid on the properties of polyvinyl alcohol and polyvinyl alcohol–cellulose composites. *Chem. Eng. J.,* 277, 242–251.

Hammood, H. Sh., Mahmood, A. S., and Irhayyim, S. S. (2019). Effect of graphite particles on physical and mechanical properties of nickel matrix composite. *Periodicals of Engineering and Natural Sciences (PEN),* 7(3), 1318.

Helen M., Viswanathan B., and Srinivasa Murthy S. (2006). Fabrication and properties of hybrid membranes based on salts of hetero-polyacid, zirconium phosphate, and polyvinyl alcohol. *J. Power Sources,* 163(1), 433–439.

Hyder M.N. and Chen P. (2009). Pervaporation dehydration of ethylene glycol with chitosan–poly (vinyl alcohol) blend membranes: Effect of CS–PVA blending ratios. *J. Membr. Sci.,* 340, 71–180.

Ibrahim M. M., El-Zawawy W. K., and Nassar M. A. (2010). Synthesis and characterization of polyvinyl alcohol/nano spherical cellulose particle films. *Carbohydr. Polym.,* 79(3), 694–699.

Irhayyim S., Sh. Hammood H., and D. Mahdi A. (2020). Mechanical and wear properties of hybrid aluminum matrix composite reinforced with graphite and nano MgO particles prepared by powder metallurgy technique. *AIMS Mater. Sci.,* 7(1), 103–115.

Jahan F., Mathad R. D., and Farheen S. 2016. Effect of mechanical strength on chitosan-PVA blends through ionic crosslinking for food packaging application. *Mater. Today Proc.,* 3(10). 3689–3696.

Jain N., Singh V. K., and Chauhan S. (2017). A review on mechanical and water absorption properties of polyvinyl alcohol-based composites/films. *J. Mech. Behav. Mater.,* 26(5–6), 213–222.

Jain N., Verma A., and Singh V. K. (2019). Dynamic Mechanical Analysis and Creep-recovery behavior of Polyvinyl Alcohol based cross-linked Bio composite reinforced with Basalt fiber. *Mater. Res. Express,* 6(10), 105373.

Jose J., Al-Harthi M. A. (2017). Citric Acid Crosslinking of Poly (Vinyl Alcohol)/Starch/Graphene Nanocomposites for Superior Properties. *Iran. Polym. J*., 26, 579–587.

Kannat S. R., Rao M. S., Chawla S. P., and Sharma A. (2012). Active chitosan–polyvinyl alcohol films with natural extracts. *Food Hydrocolloids,* 29(2), 290–297.

Kashyap S., Pratihar S. K., & Behera S. K. (2016). Strong and ductile graphene oxide reinforced PVA nanocomposites. *J. Alloy. Compd.*, 684, 254–260.

Kiro A., Bajpai J., Bajpai A. K. (2017). Designing of Silk and ZnO-Based Antibacterial and Noncytotoxic Bio-nanocomposite Films and Study of Their Mechanical and UV Absorption Behavior. *J Mech Behav Biomed Mater*., 65, 281–294.

Kuljanin J., Čomor M. I., Djoković V., and Nedeljković J. M. (2006). Synthesis and characterization of nanocomposite of polyvinyl alcohol and lead sulfide nanoparticles. *Mater. Chem. Phys.,* 95(1), 67–71.

Li H.-Z., Chen S.-C., and Wang Y.-Z. (2015). Preparation and characterization of nanocomposites of polyvinyl alcohol/cellulose nanowhiskers/chitosan. *Compos. Sci. Technol.,* 115, 60–65.

Li Y., Umer R., Samad Y. A., Zheng L., Liao K. (2013). The Effect of the Ultrasonication Pre-Treatment of Graphene Oxide (GO) on the Mechanical Properties of GO/Polyvinyl Alcohol Composites. *Carbon*, 55, 321–327.

Liang, J., Huang, Y., Zhang, L., Wang, Y., Ma, Y., Guo, T., and Chen, Y. (2009). Molecular-Level Dispersion of Graphene into Poly (vinyl alcohol) and Effective Reinforcement of their Nanocomposites. *Adv. Funct. Mater.,* 19(14), 2297–2302.

Limpan N., Prodpran T., Benjakul S., and Prasarpran S. (2010). Properties of biodegradable blend films based on fish myofibrillar protein and polyvinyl alcohol as influenced by blend composition and pH level. *J. Food Eng.,* 100(1), 85–92.

Liu K., Li Y., Xu F., Zuo Y., Zhang L., Wang H., and Liao J. (2009). Graphite/poly (vinyl alcohol) hydrogel composite as porous ringy skirt for the artificial cornea. *Mater. Sci. Eng.: C,* 29(1): 261–266.

Lu J., Wang T., and Drzal L.T. (2008). Preparation and properties of micro fibrillated cellulose polyvinyl alcohol composite materials. *Comp. Part A-Appl. S.,* 39, 738-46.

Mahardika M., Asrofi M., Amelia D., Syafri E., Mavinkere Rangappa S., and Siengchin S. (2021). Tensile Strength and Moisture Resistance Properties of Biocomposite Films Based on Polyvinyl Alcohol (PVA) with Cellulose as Reinforcement from Durian Peel Fibers. In M. Sriariyanun, Y. S. Cheng, W. Rodiahwati, & M. P. Gundupalli (Eds.). *E3S Web Conf.,* 302, 02001.

Mandal A., Chakrabarty D. (2014). Studies on the Mechanical, Thermal, Morphological, and Barrier Properties of Nanocomposites Based on Poly (Vinyl Alcohol) and Nanocellulose from Sugarcane Bagasse. *J. Ind. Eng. Chem.*, 20, 462–473.

Monjazeb Marvdashti L., Koocheki A., and Yavarmanesh M. (2017). Alyssum homolocarpum seed gum-polyvinyl alcohol biodegradable composite film: Physicochemical, mechanical, thermal and barrier properties. *Carbohydr. Polym.,* 155, 280–293.

Nagarkar R., & Patel J. (2019). Polyvinyl Alcohol: A Comprehensive Study. Acta Sci. Pharm. Sci., 3(4), 34-44.

Nasibi S., Nargesi khoramabadi H., Arefian M., Hojjati M., Tajzad I., Mokhtarzade A., Mazhar M., and Jamavari A. (2020). A review of polyvinyl alcohol / Carboxy methyl cellulose (PVA/CMC) composites for various applications. *J. Compos. Compd*., 2(3), 68–75.

Nath D. C. D., Bandyopadhyay S., Gupta S., Yu A., Blackburn D., and White C. (2010). Surface-coated fly ash used as filler in biodegradable poly (vinyl alcohol) composite films: Part 1—the modification process. *Appl. Surf. Sci.,* 256(9), 2759–2763.

Qiu K., and Netravali A. N. (2012). Fabrication and characterization of biodegradable composites based on micro fibrillated cellulose and polyvinyl alcohol. *Compos. Sci. Technol.,* 72(13), 1588–1594.

Roohani M., Habibi Y., Belgacem N. M., Ebrahim G., Karimi A. N., and Dufresne A. (2008). Cellulose whiskers reinforced polyvinyl alcohol copolymers nanocomposites. *Eur. Polym. J.,* 44(8): 2489–2498.

Sarwar, M. S., Niazi, M. B. K., Jahan, Z., Ahmad, T., Hussain, A. (2018). Preparation and Characterization of PVA/Nanocellulose/Ag Nanocomposite Films for Antimicrobial Food Packaging. *Carbohydr. Polym.*, 184, 453–464.

Sezer N., Koç M. (2019). Oxidative Acid Treatment of Carbon Nanotubes. *Surf. Interfaces*, 14: 1–8.

Shi R., Bi J., Zhang Z., Zhu A., Chen D., Zhou X., Zhang L., and Tian W. (2008). The effect of citric acid on the structural properties and cytotoxicity of the polyvinyl alcohol/starch films when molding at high temperature. *Carbohydr. Polym.,* 74(4), 763–770.

Singh K., Jain N., Verma A., Singh V. K., and Chauhan S. (2020). Functionalized Graphite–Reinforced Cross-Linked Poly (vinyl Alcohol) Nanocomposites for Vibration Isolator Application: Morphology, Mechanical, and Thermal Assessment. *Mater. Perform. Charact.,* 9(1), 20190254.

Sonker A. K., Wagner H. D., Bajpai R., Tenne R., Sui X. (2016). Effects of Tungsten Disulphide Nanotubes and Glutaric Acid on the Thermal and Mechanical Properties of Polyvinyl Alcohol. *Compos Sci Technol*., 127, 47–53.

Srinivasa P. C., Ramesh M. N., Kumar K. R., and Tharanathan R. N. (2003). Properties and sorption studies of chitosan–polyvinyl alcohol blend films. *Carbohydr. Polym.,* 53(4), 431–438.

Stone S. A., Gosavi P., Athauda T. J., Ozer R. R. (2013). In Situ Citric Acid Crosslinking of Alginate/Polyvinyl Alcohol Electrospun Nanofibers. *Mater. Lett*., 112, 32–35.

Sudhamani S. R., Prasad M. S., and Udaya Sankar K. (2003). DSC and FTIR studies on Gellan and Polyvinyl alcohol (PVA) blend films. *Food Hydrocolloids,* 17(3), 245–250.

Tabaght F.E., Azzaoui K., El Idrissi A., Jodeh S., Khalaf B., Rhazi L., Bellaouchi R., Asehraou A., Hammouti B., Sabbahi R. (2023). Synthesis, characterization, and biodegradation studies of new cellulose-based polymers, *Scientific reports,* 13, 1673, https://doi.org/10.1038/s41598-023-28298-5

Tang X., & Alavi S. (2011). Recent advances in starch, polyvinyl alcohol-based polymer blends, nanocomposites, and their biodegradability. *Carbohydr. Polym.*, 85(1), 7-16.

Tian H., Yan J., Rajulu A. V., Xiang A., and Luo X. (2017). Fabrication and properties of polyvinyl alcohol/starch blend films: Effect of composition and humidity. *Int. J. Biol. Macromol.,* 96: 518–523.

Tsuda M. (1963). Schotten-Baumann esterification of poly (viny1 alcohol). II, *Mol. Chem. Phys.*, 72, 183-190.

Vesali Naseh A. A., Khodadadi Y., Mortazavi O., Alizadeh Sahraei F., Pourfayaz S., Mosadegh Sedghi. (2009). Functionalization of Carbon Nanotubes Using Nitric Acid Oxidation and Dbd Plasma. Zenodo.

Wang S., Ren J., Li W., Sun R., Liu S. (2014). Properties of Polyvinyl Alcohol/Xylan Composite Films with Citric Acid. *Carbohydr. Polym.*, 103, 94–99.

Wang Y., & Hsieh Y. L. (2010). Crosslinking of polyvinyl alcohol (PVA) fibrous membranes with glutaraldehyde and PEG diacyl chloride. *J. Appl. Polym. Sci.*, p. NA-NA.

Watanabe Y., Hamada N., Morita M., & Tsujisaka Y. (1976). Purification and properties of a polyvinyl alcohol-degrading enzyme produced by a strain of Pseudomonas. *Arch. Biochem. Biophys.*, 174(2), 575–581.

Xu X., Yang Y.-Q., Xing Y.-Y., Yang J.-F., and Wang S.-F. (2013). Properties of novel polyvinyl alcohol/cellulose nanocrystals/silver nanoparticles blend membranes. *Carbohydr. Polym.*, 98(2), 1573–1577.

Yang, E., Qin, X., & Wang, S. 2008. Electrospun crosslinked polyvinyl alcohol membrane. *Mat. Lett.*, 62(20), 3555–3557.

Ye D., Jiang L., Hu X., Zhang M., Zhang X. (2016). Lignosulfonate as Reinforcement in Polyvinyl Alcohol Film: Mechanical Properties and Interaction Analysis. *Int. J. Biol. Macromol.*, 83, 209–215.

Zhang W., Yang X., Li, C., Liang M., Lu, C., and Deng Y. (2011). Mechanochemical activation of cellulose and its thermoplastic polyvinyl alcohol eco composites with enhanced physicochemical properties. *Carbohydr. Polym.,* 83(1), 257–263.

Zhao X., Zhang Q., Chen D., Lu P. (2010). Enhanced Mechanical Properties of Graphene-Based Poly (Vinyl Alcohol) Composites. *Macromolecules*, 43, 2357–2363.

Zhou J., Ma Y, Ren L., Tong J., Liu Z., Xie L. (2009). Preparation and Characterization of Surface Cross-linked TPS/PVA Blend Films. *Carbohydr. Polym.*, 76, 632–638.

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