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INNOVATIONS IN POLY(VINYL ALCOHOL) DERIVED NANOMATERIALS

ABSTRACT

Poly(vinyl alcohol) (PVA) has been considered as an important commercial synthetic thermoplastic polymer. PVA is a low cost, reasonably processable, optically transmitting, heat stable, and mechanically robust plastic. PVA-based nanomaterials usually comprise of the nanocomposites (PVA/graphene, PVA/carbon nanotube, PVA/nanodiamond, PVA/metal nanoparticle) and nanofibers. The structural, optical, mechanical, and electrical properties of the PVA-based nanomaterials have been enhanced with nanofiller addition or nanostructuring. This review offers fundamentals and advanced aspects of poly(vinyl alcohol) and the derived nanomaterials. It highlights recent advances in PVA nanocomposites and nanofibers for potential applications. The PVA-based nanomaterials have been successfully employed in fuel cells, sensors, batteries, membranes, electronics, and drug delivery relevances. The challenges and opportunities to strengthen the research fields of PVA-based nanomaterials have also been presented.

Keywords: PVA; nanocomposite; nanofiber; graphene; fuel cell

INTRODUCTION

Poly(vinyl alcohol) (PVA) is a synthetic thermoplastic polymer having water solubility [1, 2]. It is represented as $[\text{CH}_2\text{CH}(\text{OH})]_n$. It is a low cost and easily processable polymer [3-5]. Commercial production of PVA is usually attained via vinyl acetate monomer [6, 7]. PVA is susceptible to partial or complete hydrolysis, which may affect the final polymer properties [3]. Hydrogen bonding between PVA chains is often responsible for the semicrystalline nature of this polymer [8]. PVA has good water solubility, thermal stability, corrosion resistance, and optical transmission [9]. Different morphologies of PVA have also proven useful for pharmaceutical and

biomedical characteristics. PVA has found applications in number of fields including membranes, coatings, adhesives, sensors, batteries, fuel cells, textiles, paper making, and biomedical frameworks [10-16]. Attempts have been made to form PVA nanocomposites to increase their span in technical arenas [17]. Different types of nanofillers have been incorporated in PVA matrix to enhance the structural, optical, electrical, and mechanical properties of this versatile polymer [18]. In this review, various prospects of PVA nanocomposites and other nanomaterials have been comprehended. Especially, the physical properties and applications of various PVA nanocomposites and nanofibers have been discussed. PVA has been reinforced with nanocarbon and inorganic nanofillers to broaden the prospects of these materials for technical applications such as fuel cells, batteries, membranes, sensors, electronics and drug delivery. Such nanocomposites have found future potential for efficient commercial materials.

POLY(VINYL ALCOHOL)

Poly(vinyl alcohol) (PVA) is a white colored odorless synthetic thermoplastic polymer. It exists in powdered or granular form [18]. It is a nontoxic and biocompatible polymer [1]. It has excellent dielectric, optical, and charge storage properties [19]. Table 1 shows physical properties of neat PVA. This polymer has wide ranging applications in adhesives, coatings, electronics, construction, textiles, paper, and biomedical industries [20, 21]. Usually, vinyl acetate monomer is used for the commercial production of PVA. In alkaline conditions, the ester groups of poly(vinyl acetate) are substituted with hydroxyl groups to form PVA. Polymerization of poly(vinyl acetate) occurs at low temperatures (-80 °C to -20 °C) [3, 22, 23]. During thermal degradation, weight loss of PVA is observed between 100-200°C owing to loss of moisture and backbone cleavage. Doping of PVA with nanofillers has resulted in significant improvements in adhesive, optical, electrical, and mechanical characteristics of the nanocomposites [4, 24, 25].

Table 1. The physical properties of pure PVA

Property	Value
Form	White
Density	1.19-1.31 gcm ⁻³
Thermal stability	100, 150, 200 °C
Melting point	230 °C
Glass transition temperature	75-85 °C
Specific heat	1.5 J/(gK)
Refractive index	1.47
Dielectric constant	12.06 (50 Hz, 140 °C)
Charge storage	1.91×10 ⁻⁶ F

POLY(VINYL ALCOHOL) DERIVED NANOMATERIALS

PVA-based nanocomposite

The PVA-based nanocomposites have been developed using various nanofillers [18, 26-28]. The nature, shape, and content of nanofillers may affect the PVA-based nanocomposite properties [29, 30]. The organic or inorganic nature of nanofiller such as melt oxide nanoparticles or nanocarbons (carbon nanotube, graphene, etc.) modify the physical properties of PVA according to their reinforcing efficiency. Similarly, the nanofiller content affects the dispersion properties of nanoparticles and also the mechanical and thermal properties. The 0, 1, 2, and 3-dimensional nanomaterials have been used as nanofillers in polymers [31]. Usually, the nanofillers <5 wt.% are effective to enhance the thermal conductivity, electrical conductivity, dimensional stability, strength, and modulus of the PVA nanocomposites [32]. In this regard, nanocarbon nanofillers have large surface area to better interact with the polymeric materials [33, 34].

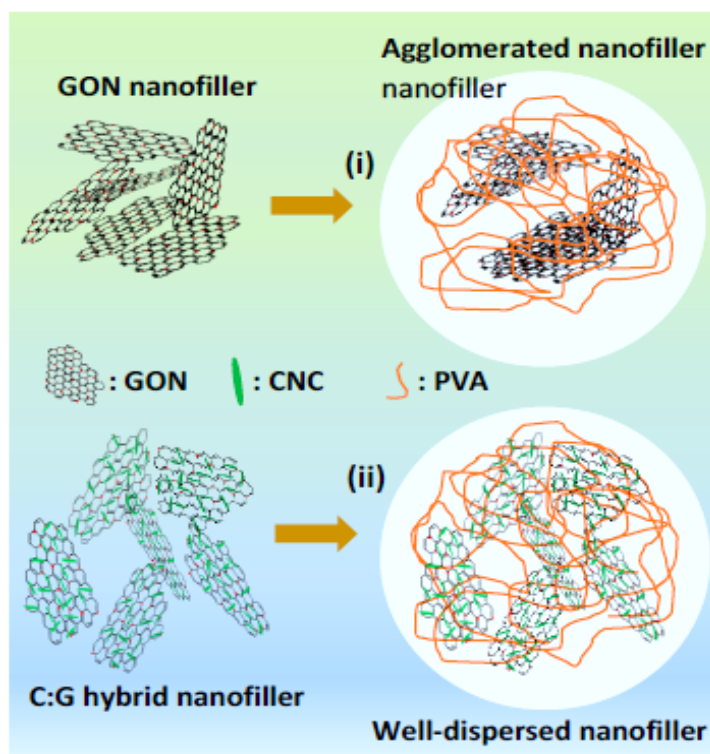


Fig. 1. Schematic of dispersion state of (i) GON and (ii) C:G hybrid nanofillers within PVA matrix [35]

The PVA/graphene and PVA/graphene oxide nanocomposites have been designed. In this regard, various synthesis methods have been used to obtain high performance PVA nanocomposites with graphene or graphene oxide nanofillers. El Miri N et. al. [35] formed hybrid nanofillers with cellulose nanocrystals (CNC) and graphene oxide nanosheets (GON) referred as C:G in various ratios (2:1, 1:1 and 1:2). Aggregation may occur in the PVA/GON nanocomposite system given in Fig. 1(i). Conversely, the hybrid system of C:G nanofiller had homogeneous dispersion (Fig. 1b(ii)). Fine dispersion may be due to the hydrogen bonding interactions between

PVA and C:G. The PVA nanocomposite with 5wt.% hybrid nanofiller (1:2) enhanced the Young's modulus and tensile strength by 320% and 124%, respectively, relative to neat PVA. Another important strategy used to enhance the properties of PVA nanocomposite is the incorporation of inorganic nanoparticle decorated graphene or GO nanofillers. Zhang et. al. [36] produced magnetic nanoparticle-attached graphene oxide (GO@Fe₃O₄). The nanofiller was reinforced in PVA matrix. The 0.3 wt.% GO@Fe₃O₄ enhanced the failure strain to 237% in PVA/GO@Fe₃O₄, relative to neat PVA (72%). The effect of mechanical property improvement was dedicated to the incorporation of inorganic nanoparticle decorated GO in PVA. The magnetic nature of iron nanoparticles was useful to enhance the superparamagnetic behavior of the nanocomposites. The PVA/GO@Fe₃O₄ had also improved thermal stability, relative to PVA.

The graphene-based nanofillers have been efficiently employed to enhance the thermal and mechanical properties of PVA nanocomposites, relative to unfilled PVA matrix [37-40]. Graphene is also found to be advantageous in PVA property enhancement, as compared with carbon nanotubes.

The PVA matrix has also been reinforced with carbon nanotubes (CNTs). Chen et. al. [41] reinforced multi-walled carbon nanotube (MWCNT) in poly(vinyl alcohol) matrix. Inclusion of 9.1 wt.% MWCNT increased the tensile strength and Young's modulus to 2.7 and 4.5, respectively. Hung et. al. [42] prepared PVA and poly(vinyl pyrrolidone) (PVP) functional MWCNT. Addition of PVP treated MWCNT enhanced the mechanical properties of the nanocomposite (Fig. 2). Neat PVA had tensile strength of 1.8MPa. Addition of 1wt.% PVP-MWCNT enhanced the tensile strength to 4.2 MPa. Inclusion of 0.5-2 wt.% nanofiller improved the elastic modulus from 1.5 to 2.5 MPa. The use of functional carbon nanotube nanofiller is quite advantageous to enhance the mechanical properties. However, as compared to the graphene nanofillers, carbon nanotubes have sometimes been found to be less efficient [36, 37]. The obvious reason of declined physical properties relative to polymer/graphene is the nanotube aggregation in PVA matrix.

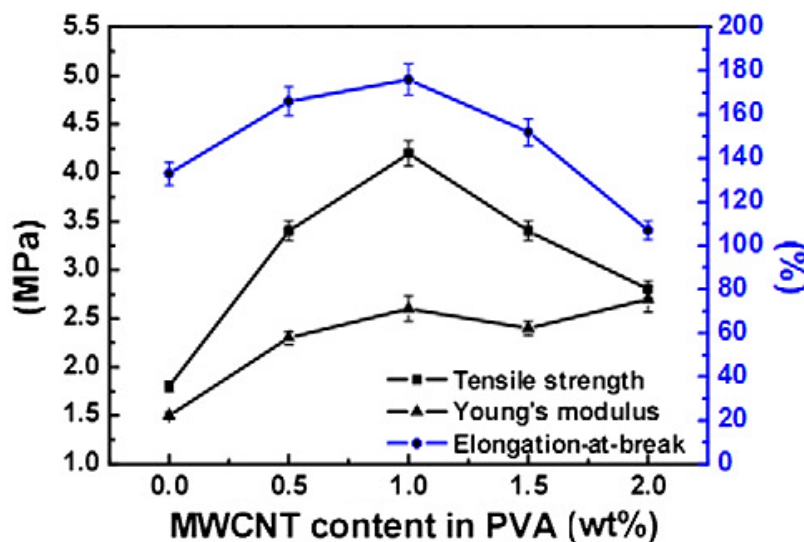


Fig. 2. Comparison of tensile elastic modulus, tensile strength, and elongation at break of the composite hydrogels as a function of MWCNT content [42]

The poly(vinyl alcohol) and nanodiamond (ND)-based nanocomposites have also been identified as an important category. Angjellari et. al [43] used detonation nanodiamond (DND) to fill the PVA matrix. The 0.5-5 wt.% DND loaded nanocomposites have been prepared. Inclusion of 5 wt.% DND enhanced the indentation modulus to 200%. The PVA/DND nanocomposite had well-dispersed nanoparticles in the matrix. Varga et. al. [44] proposed a model describing interactions between PVA and ND (Fig. 3). According to this model, the PVA molecules may form hydrogen bonding to the hydrophilic surface of ND. Release of free OH^- increases owing to decrease in zeta potential of ND upon ultrasonication in PVA solution.

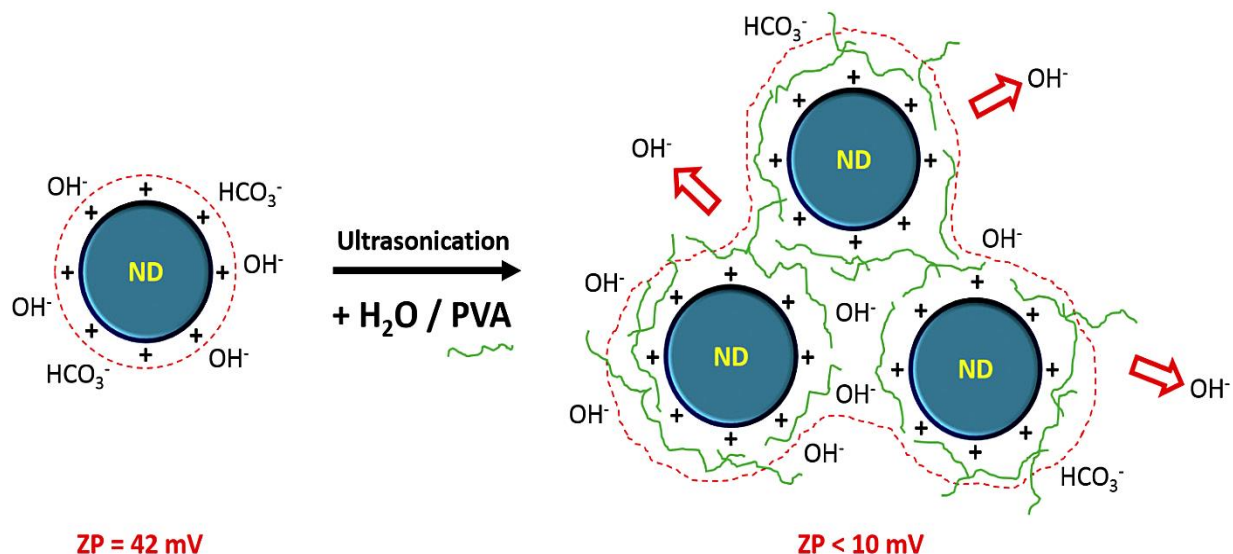


Fig. 3. Schematic model describing interaction of ND and PVA [44]

PVA nanocomposites with metal oxide nanoparticles have also been reported [45, 46]. Mandal et. al. [47] filled PVA with Fe (II) and Fe (III) oxides. The 10 wt.% iron oxide loading enhanced the flux, selectivity, and pervaporation separation index, relative to the neat PVA. Roy et. al. [48] has filled PVA with zinc oxide (ZnO) nanoparticles. The dielectric property relies on the conductivity of nanocomposites. Inclusion of ZnO impeded the electron movement, and so enhanced the dielectric properties of these materials. The optical properties of the nanocomposites were also improved with nanoparticle addition, relative to neat PVA. In conclusion, PVA with nanocarbon nanofillers has shown enhanced thermal and mechanical properties. Inclusion of inorganic nanoparticles have enhanced the optical, dielectric, and membranes properties of the nanocomposites [49]. Thus, these materials have been employed in optoelectronic devices, superparamagnetic structures, strengthened and heat stable aerospace materials, and enhanced dielectric permittivity materials [50, 51].

PVA-based nanofibers

Electrospinning has been considered as a modest method for nanofiber preparation. This method has been applied for various polymers including PVA [52]. Electrospinning has been used to form ultrafine fibers of <100 nm diameter. This method involves using polymer solution or polymer melt. The archetypal electrospinning set up is given in Fig. 4. Commonly used

systems are the vertical and horizontal ones. The electrospinning system usually consists of a spinneret, high voltage power supply, and collecting plate. The liquid jet is ejected through the capillary spinneret under high voltage [53].

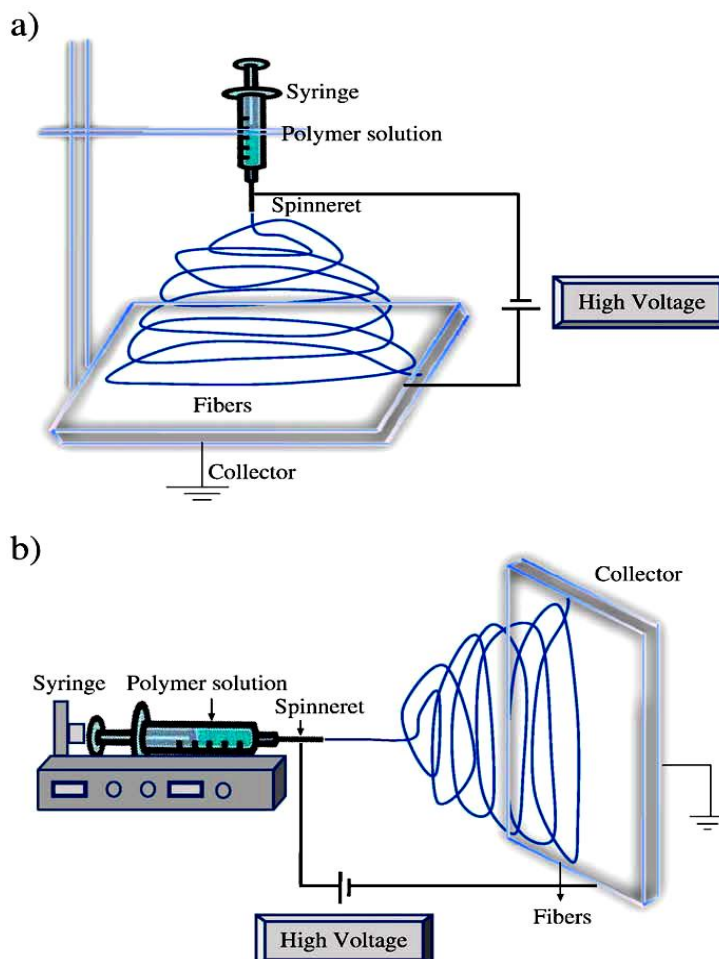


Fig. 4. Schematic diagram of electrospinning set up (a) typical vertical set up and (b) horizontal set up of electrospinning apparatus [52]

The charged surface of the ejected polymer jet is attracted towards the collector. The electrospun nanofibers are collected on the collecting plate. Electrospinning has been used to form nanocomposite nanofibers [54, 55]. Electrospinning technique has been used to reinforce the PVA nanofibers with nanocarbon nanofillers and metal nanoparticles. Owing to good fiber formation properties of PVA and PVA-based nanocomposites, these materials are useful for membranes and coatings [5, 56-60]. Poly(vinyl alcohol) is a water soluble polymer, so it has successfully been used to produce nanocomposite nanofibers [61-64]. For electrospinning, a solvent is usually used to dissolve the desired polymer. Then, the polymer solution is used to form the polymer fibers under the influence of electrostatic force. During fiber formation, the solvent is evaporated. In this regard, water is an inert, environmentally-friendly, and inexpensive solvent. Thus, PVA is an advantageous polymer i.e. easily dissolved in water and processed. The

hydroxyl groups of PVA has been found accountable for the hydrophilicity of nanofibers [65]. This hydrophilic polymer is easily soluble in water and can be used for electrospinning. PVA is also used to reduce the surface tension of the solution, so processability becomes easy. Poly(vinylalcohol)-based nanocomposite nanofibers have been prepared *via* combining the electrospinning and sol-gel techniques [66]. As, PVA is a biocompatible polymer owing to *in situ* or *ex situ* non-toxicity. The biocompatible nature of PVA nanofibers render them useful for biomedical applications such as tissue engineering, bioimplants, etc. [28]. Hence, PVA nanofibers have fine processability, hydrophilicity, and biocompatibility for biomedical engineering.

Abd El-aziz et. al. [67] developed PVA and hydroxyapatite (HA) nanocomposite nanofibers using electrospinning process. Glutaraldehyde was used to cross-link the nanofibers. Glutaraldehyde is a dialdehyde. During cross-linking, the hydroxyl groups of the PVA and the aldehyde groups of glutaraldehyde react in the presence of strong acid to form covalent bonding. The cross-linking was beneficial because it enhanced the mechanical properties and insolubility of PVA fibers. In this way, the PVA and nanocomposite fibers can be used for water filtration applications. Scanning Electron Microscopy (SEM) was used to analyze the morphology of the PVA/HA nanocomposite nanofibers (Fig. 5). The nanofibers were found oriented in axial direction. The spherical HA nanoparticles were found dispersed on the individual nanofibers. The energy-dispersive X-ray (EDX) was used to analyze the elemental composition of the nanofibers.

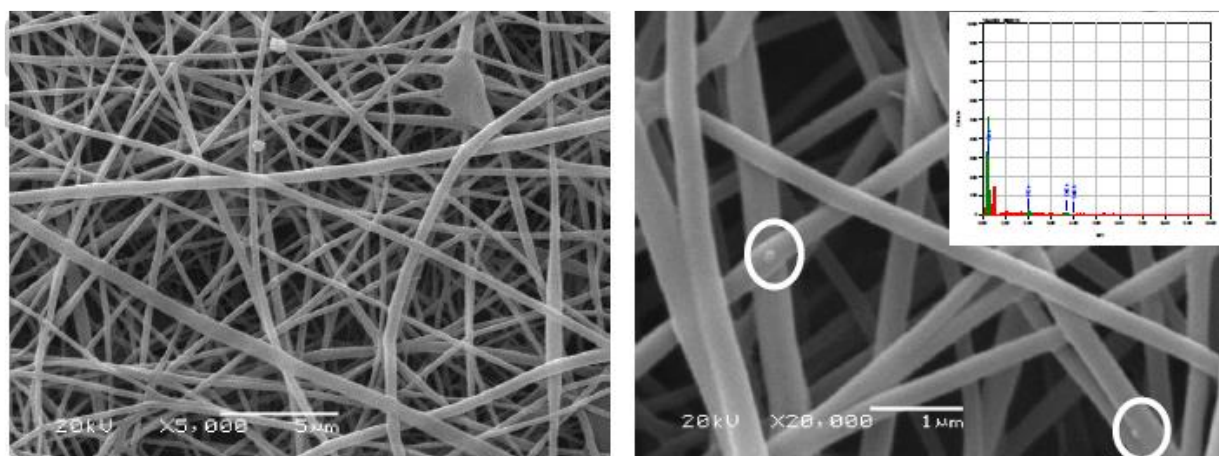


Fig. 5. SEM images and EDX composition of the elements of PVA/(1%) HA nanofibers [67]

Wang et. al. [68] formed PVA nanofibers with ZnS:Cu. The nanofibers were studied for luminescence, crystalline, and morphology properties. Puguan et. al. [69] produced cross-linked electrospun PVA membranes. The nanofibers had diameter of 260 ± 61 nm. SEM micrographs of crosslinked PVA membrane is given in Fig. 6. The crosslinking density and degree of swelling of the membranes were also studied.

Wu et. al. [70] prepared thiol-functional mesoporous poly(vinyl alcohol)/SiO₂ nanocomposite nanofibers. The functional PVA/SiO₂ nanocomposite nanofibrous membranes had high Cu²⁺ ion adsorption capacity of 489.12 mg/g owing to surface area >290 m²/g. The membranes were promising materials for heavy metal ion removal from water.

Hence, PVA nanocomposite nanofibers have been formed using electrospinning method and used for various applications including metal ion removal, separation, and structural materials.

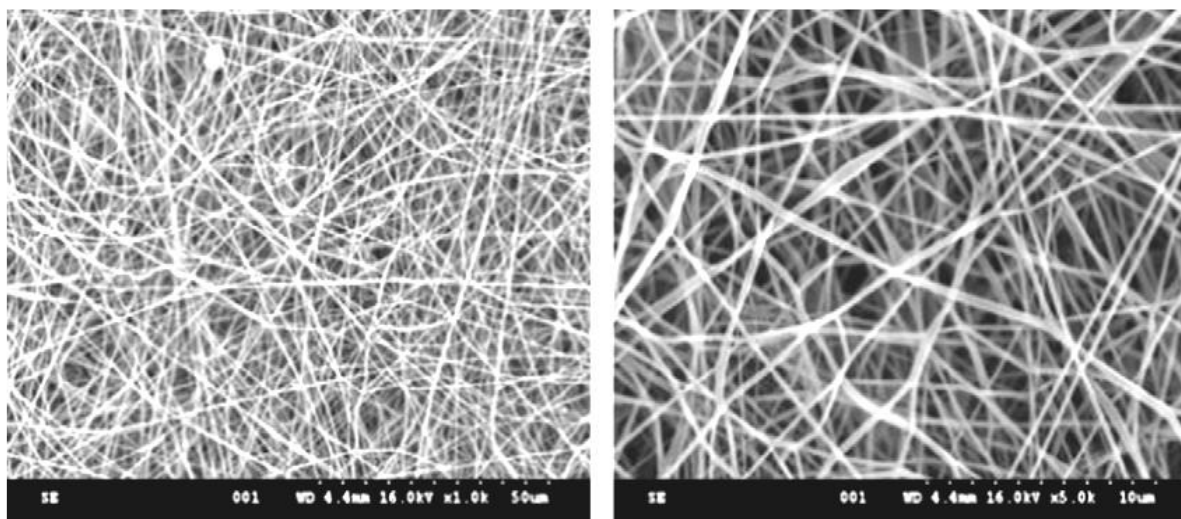


Fig. 6. Surface SEM images of electrospun PVA substrate in (a) 1 K and (b) 5 K magnification [69]

APPLICATIONS OF POLY(VINYL ALCOHOL)-BASED NANOMATERIALS

Fuel cells are facile energy sources having light weight, environmental friendliness, and low CO₂ emission. Direct-methanol fuel cell or (DMFC) is a category of proton-exchange fuel cells, in which methanol is used as a fuel. The foremost benefit of using methanol fuel is the ease of methanol transport in diverse environmental conditions. Use of methanol as a general energy transport medium enhances the power density and fuel cell efficiency of DMFC [71]. In these fuel cells, efficient proton-exchange membranes are also used to enhance the conductivity and cell performance. In these fuel cells, efficient membranes having high methanol permeability are desirable. PVA-based proton exchange membranes have been developed for DMFC. The PVA membranes having low fuel permeability and high ionic conductance may lead to high fuel cell efficiency and power density. Inclusion of nanoparticles in PVA membranes also enhances the membrane performance. Methanol permeability is an important parameter to DMFC. The lower methanol permeability of DMFC depicts high fuel utilization efficiency. The DMFC fuel cell is usually modified to obtain high power density (amount of power per unit fuel volume). The methanol fuel causes high power density of fuel cells. The PVA and silica nanoparticles have been used as solid electrolyte for DMFC [72]. Addition of silica nanoparticles enhanced the membrane strength, stability, and permeability. The PVA/CNT nanocomposite-based DMFC membranes possess high ionic conductivity and reduced methanol permeability [73]. The power density of the fuel cell was observed as 39-87 mWcm⁻². Li et. al. [74] proposed quaternized poly(vinyl alcohol) (QPVA) and chitosan nanoparticle-filled quaternized poly(vinyl alcohol) (CQPVA). The CQPVA was used as a membrane in DMAFC (Fig. 7). Inclusion of nanoparticles in proton exchange membranes usually facilitates the ionic transport through the membranes.

Addition of 10% chitosan nanoparticles enhanced the ionic conductivity and reduced the methanol permeability of the CQPVA membranes. The power density of the fuel cell was found as 67 mWcm^{-2} .

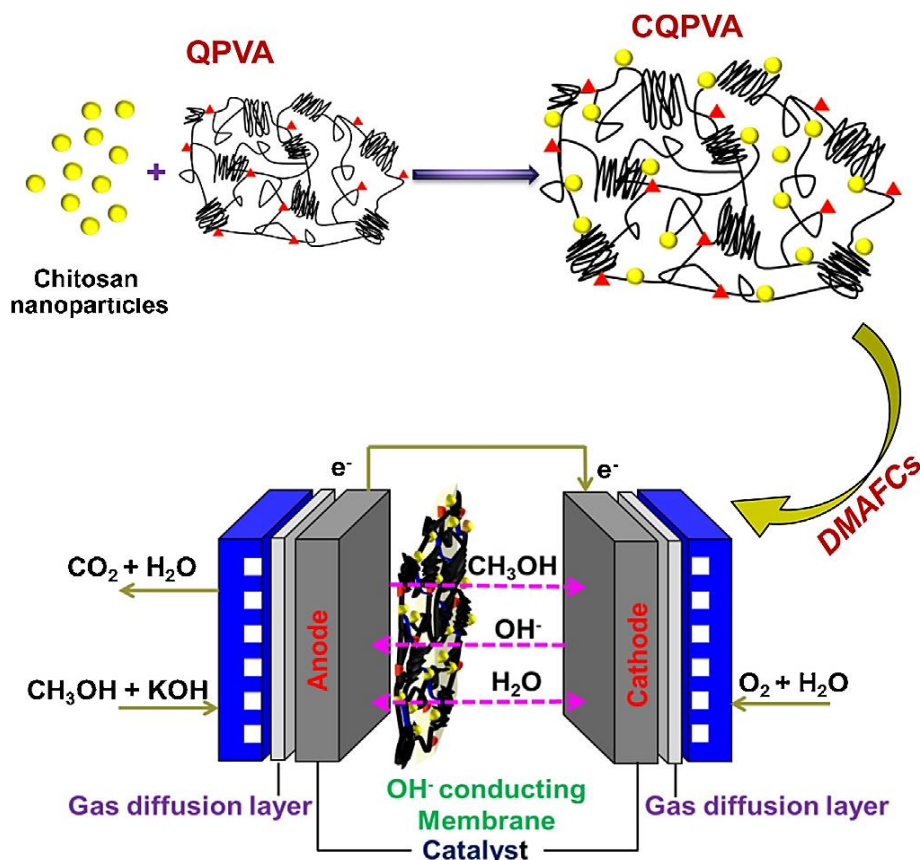


Fig. 7. Schematic of glutaraldehyde cross-linked chitosan nanocomposite membranes for direct alkaline methanol fuel cell [74]

The PVA-based nanocomposites have been tested for sensor applications. Chirizzi et. al. [75] introduced CuO nanowires of 120-170 nm in PVA matrix. The material was used to form amperometric nonenzymatic H_2O_2 sensor. The electrodes had large current density to reduce H_2O_2 . The sensor has shown high sensitivity, reproducibility, and low detection limit. The morphological and electrochemical properties of PVA-based nanocomposite sensors have shown superior performance [76, 77].

The PVA-based nanofibrous membranes have been used for toxic ion removal from polluted water. The PVA/silver nanoparticle membranes have been used for this purpose [78]. Filippo et. al. [79] designed poly(vinyl alcohol)/silica nanoparticle (PVA/ SiO_2)-based nanocomposite nanofibrous membranes for Cu^{2+} adsorption. The mechanism for the adsorption of Cu^{2+} ions on the membrane is given in Fig. 8. The mechanism involves the electrostatic interaction i.e. ionic interactions between the positively charged metal ions and negatively charged PVA and lone-pair electron donation to the matrix [70]. The PVA/ SiO_2 offers low cost and efficient membranes for toxic heavy metal ion removal.

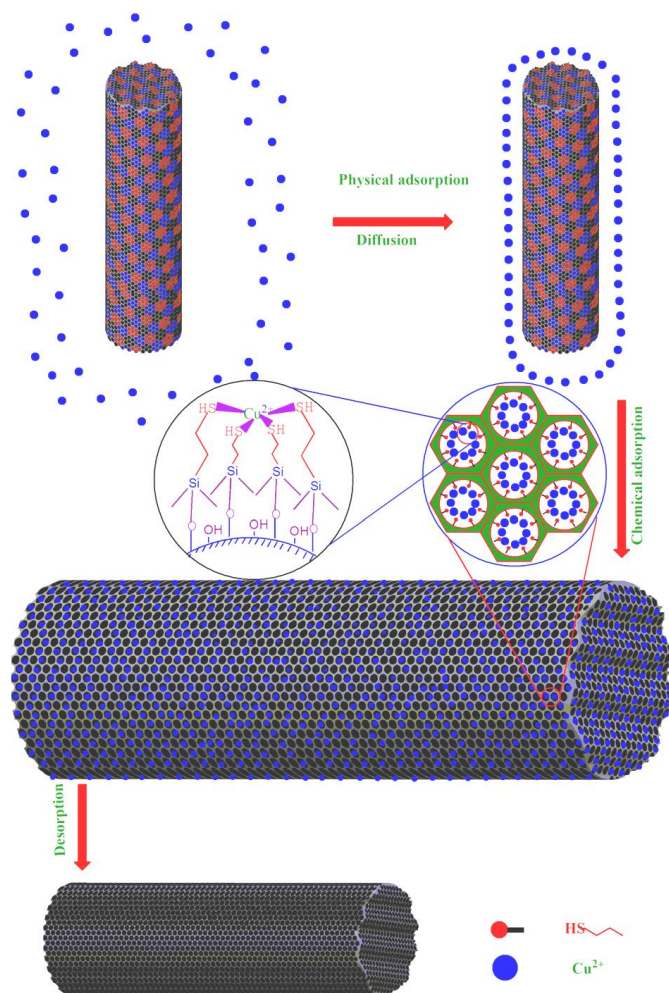


Fig. 8. The mechanism of Cu^{2+} adsorption on PVA/SiO₂ composite nanofiber [70]

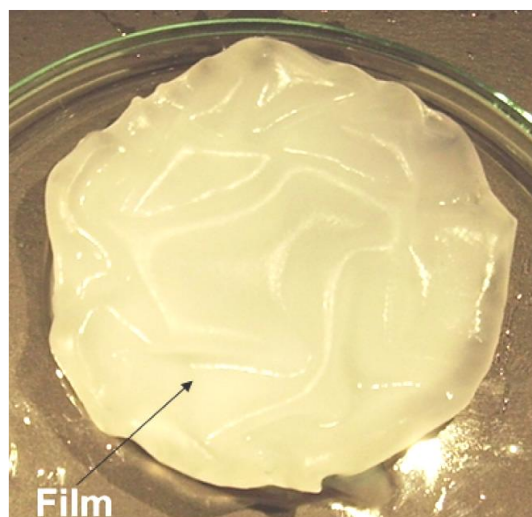


Fig. 9. Composite with film on upper surface [84]

The PVA-based nanocomposites have also been focused for drug-release applications [80, 81]. The bioadhesive nature of these materials are useful in this regard. The PVA gel carriers have been used for controlled release of drugs [82, 83]. Nugent et. al. [84] prepared cross-linked poly(vinyl alcohol)-based nanomaterials. The nanocomposites have shown high physical strength and localized controlled drug delivery. Fig. 9 shows the PVA-based nanocomposite film. The micro-thermal analysis was used to study the gel microstructure. The PVA-based nanocomposite coatings have also been used for implantable devices [85].

FUTURE STANDPOINTS AND SUMMARY

Table 2 summarizes few essential PVA nanocomposite systems discussed in this review. Various nanofillers have been incorporated in PVA matrices to enhance the physical properties and technical performance. The PVA-based nanomaterials have found applications in various technical fields [86]. These nanomaterials have opened new possibilities for fuel cells, sensors, membranes, and biomedical sectors. Future research on PVA-based nanomaterials must focus new design variations through tailoring their physicochemical properties [87, 88].

Table 2. Specific properties of few PVA nanocomposites

Matrix	Nanofiller	Property/application	Ref.
PVA	Graphene oxide, cellulose nanocrystals	Mechanical properties	[35]
	Magnetic nanoparticle-attached graphene oxide	Mechanical properties	[36]
	Carbon nanotube	Mechanical properties	[41]
	Carbon nanotube	Mechanical properties	[42]
	Nanodiamond	Indentation modulus	[43]
	Nanodiamond	zeta potential	[44]
	Fe (II) and Fe (III) oxides	Membrane selectivity, flux	[47]
	ZnO	Dielectric property	[48]
	Hydroxyapatite	Mechanical properties, membrane performance	[67]
	SiO ₂	Metal ion removal	[70]
	Chitosan nanoparticle	Fuel cell membrane	[74]
	CuO nanowires	H ₂ O ₂ sensor	[75]
	Silica nanoparticle	Membranes for ion adsorption	[79]

One of the main challenges to form high performance PVA related materials is the development of new synthesis methodologies [89, 90]. Moreover, the use of unexplored nanofillers and modified nanoparticles may improve the nanocomposite performance. To achieve interfacial interactions and controlled morphologies in PVA-based nanomaterials are also challenging factors [91]. Very few attempts have been seen regarding the PVA nanocomposite in

DMFC membranes and electrolytes. Novel nanofibrous membrane have been used to reduce the methanol permeability, and enhance the power density and cell performance. The PVA-based nanomaterials offered promising platform for the development of innovative amperometric nonenzymatic H_2O_2 sensor [92-94]. However, facile miniaturization of these sensing devices need to be focused in future [95-97]. Further research on PVA-based nanofibrous membranes are promising materials for heavy metal ion removal and recovery [98]. The PVA-based nanocomposites must be engrossed for better crystallinity, adhesiveness, and controlled drug release. Research may also reveal high performance biomedical tissue engineering implants [99, 100].

In few words, PVA-based nanocomposites and nanofibers have been reviewed in this article. The nanocarbon nanofillers and metal nanoparticles have been reinforced in PVA matrix. The PVA/nanocarbon materials had resulted in enhanced mechanical, thermal, electrical, optical, permeability, and morphological features of these materials. The physical properties, fabrication, and applications of these materials have been methodically reviewed. Progress in PVA-based nanocomposites have revealed solicitations in fuel cells, sensors, membranes, drug delivery, biomedical implants, coatings, adhesives, electronics, and other applications.

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