

Naman Jain*, Vinay Kumar Singh and Sakshi Chauhan

A review on mechanical and water absorption properties of polyvinyl alcohol based composites/films

<https://doi.org/10.1515/jmbm-2017-0027>

Abstract: Polyvinyl alcohol (PVA) is a nontoxic and thermoplastic polymer which is completely biodegradable. PVA shows excellent mechanical and thermal properties due to better interfacial adhesion with reinforcing material such as fibers, particles or flakes because of which it can be used for fabrication of composite. PVA based fiber or particle reinforcing composites have gained interest in many applications in different fields. This paper reviews the mechanical and water absorption properties studied by different researcher and some of them were discussed here. The article also focused on the effect on the mechanical properties on PVA based composites with particle or fiber used as reinforcing material at nano/micro level and different polymers used to prepare PVA blend films. The major disadvantage of PVA based composites/films is higher water uptake or solubility in water. To over this negative aspect, many researchers studied crosslinking of PVA based composites/films, which are also discussed in the article. This review concludes that PVA has the potential for use in the synthesis of composites/films with their abundant applications.

Keywords: crosslinking; mechanical properties; nano-composite; polyvinyl alcohol; water absorption.

1 Introduction

Synthetic and natural are two main classifications of polymers. Starch, chitin, protein, Lignin, shellac, cellulose etc. come under natural polymer whereas poly(amides) [1], poly(anhydrides), poly(amide-enamines) Poly(vinyl alcohol), poly(ethylene-co-vinyl alcohol), poly(vinyl acetate), polyesters, poly(glycolic acid), poly(lactic acid),

poly(caprolactone), poly(ortho esters) etc. come under synthetic polymer. Ecological concerns such as recyclability and environmental safety have resulted in renewed attention in the natural polymer resin. As compared with petroleum [2] based thermoset plastics which are toxic and non-biodegradable. Biodegradable polymers decomposed by the action of microorganisms converted into the form of H_2O and CO_2 . These H_2O and CO_2 are absorbed into the plant systems. Other environmental benefits of bio-based polymers include low embodied energy, CO_2 sequestration, reduced depletion of fossil-based resources and an optimistic impact on agriculture. Due to increase in the awareness of environmentally sustainable technology demand of bio-composite or green composite material have received significant interest in past few year. As per the market survey, there are 235 million tons polymer production was found for 2011 and out of which bio-based polymer share about 1.5% i.e. 3.5 million tons which are going to be increase by 3% at end of 2020. Polyvinyl alcohol (PVA) also known as polyethenol, most commonly used polymer as an adhesive product and making other polymers. PVA is cheap and easily available polymers exist in white powder form.

Polyvinyl alcohol (PVA) chemical formula shown in Figure 1 is synthetic biodegradable thermoplastic polymer [3] which is nontoxic and has application in different fields such as resins, medical, building industry, packaging materials etc. Herman and Haehnel in 1924 [4] were first to prepare PVA from polyvinyl esters. After 2 year it was used in textile industry in Germany. The expansion of application of PVA has been prompted largely in other area such as: in 1951 Levine et al. [5] studied use of PVA as plumbage material for thoracic surgery; in 1979 Sumita et al. [6] prepared the semiconducting CuI surface layer by coagulation of polymer $-Cu^2$ complexes in PVA and polyacrylamide; in 1986 Tamura et al. [7] developed gelling polyvinyl alcohol and their medical use was examined; Hirai in 1994 investigated gel of PVA highly swollen with dimethyl sulfoxide as a gel actuator; Xu et al. [8] studied the crosslinking systems between bifunctional aldehydes and PVA to improve the paper wet strength; in 2011 Patil et al. [9] synthesized PVA/polyaniline (PANI) thin films for supercapacitor application; Stefani et al. [10] develop

*Corresponding author: Naman Jain, Department of Mechanical Engineering, G. B. Pant University of Agriculture and Technology, Pantnagar, India, e-mail: namanjainyati@gmail.com

Vinay Kumar Singh and Sakshi Chauhan: Department of Mechanical Engineering, G. B. Pant University of Agriculture and Technology, Pantnagar, India

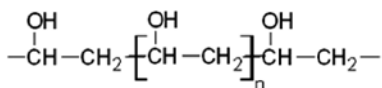


Figure 1: Chemical formula of polyvinyl alcohol.

and characterize a time temperature indicator (TTI) based on a PVA/Chitosan polymeric doped with anthocyanins in order to indirectly indicate food quality changes and applications of PVA are shown in Table 1.

2 PVA based film/composite

In this section review of mechanical properties and water absorption capacity of PVA based film/composite has been done from last 10 to 12 year. Due to better interfacial adhesion between the PVA matrix and fiber PVA composites were mechanically stronger and tougher and have a potential for use in several applications. PVA is completely soluble in water due to the presence of free hydroxyl groups in the polymeric matrix which is the disadvantage of PVA based film/composite, therefore, water absorption capacity tests are one of the major design criteria.

2.1 Mechanical properties of PVA based composites/films

Better interfacial adhesion between the PVA matrix and fibers, fiber reinforced PVA composites were mechanically stronger and tougher than the PVA film which results in wide application of PVA for composite material. Kiro et al. [23] prepared sericin and PVA based composite in which ZnO nanoparticles were impregnated. Vickers hardness values were found to be 15.11, 16.46, 17.39, 18.71 and 20.09 kg/mm² on varying the amount of ZnO nanoparticles to 200, 250, 300 and 350 mg, respectively. Sonker et al. [24] fabricated PVA based crosslinked composite in which structural modification was done by glutaric acid (GA) and reinforced with tungsten disulfide nanotubes nanoparticle (WSNTs). Three types of PVA films were prepared, i.e. neat PVA, thermally crosslinked PVA (TH-CL-PVA) and glutaric acid crosslinked PVA (GA-CL-PVA) and in each type, WSNT was added as reinforcement. SEM image of WSNT-PVA composite is shown in Figure 3A. It was found that WSNT-TH-CL-PVA shows the maximum tensile strength of 139.9 MPa with Young's modulus of 7.1 GPa and WSNT-GA-CL-PVA shows maximum toughness of 85.68 MPa. In 2015 Guzman-Puyol

et al. [25] studied the effect of trifluoroacetic acid (TFA) on PVA and PVA-cellulose composite. The neat PVA film has Young's modulus 2.75 GPa with 57% of elongation whereas PVA-TFA film has Young's modulus 25 MPa with elongation of 693% from above result it was concluded that TFA act as the plasticizer. In 2013 Li et al. [26] studied the effect of ultrasonication on graphene oxide (GO)/PVA composite. The GO suspension obtained was diluted to 5 mg/ml and then ultrasonicated for 0–5 h were added to 10 wt.% PVA DI water solution. Tensile property of GO-PVA is 12.6% higher than neat PVA film and maximum strength is 82.5 MPa for 30 min ultrasonication. In 2013 Li et al. [26] studied the effect of ultrasonication on graphene oxide (GO)/PVA composite The GO suspension obtained was diluted to 5 mg/ml and then ultrasonicated for 0–5 h were added to 10 wt.% PVA DI water solution. Tensile property of GO-PVA is 12.6% higher than neat PVA film and maximum strength is 82.5 MPa for 30 min ultrasonication. In 2010 Ibrahim et al. [27] synthesized PVA based film in which nanospherical cellulose obtained from cotton linter and bleached linen were used as reinforcement particles. Tensile strength of bleached linen composite was increased up to 20 wt.% whereas the strength of composite decrease with the presence of cotton linter. Ching et al. [28] in 2010 fabricated polyvinyl alcohol based composite in which cellulose nanocrystals and nanosilica were used as a reinforcement material. To prepared the films 10 wt.% PVA solution with water was stirring the solution at 90°C for 2 h and after cooling to room temperature nanocrystals cellulose (1–7 wt.%) and nanosilica (0.5%) were added. Mechanical testing of PVA based film is done. The Young's modulus increases with increasing the NCs content. The Young's modulus of PVA films without CNs was 15.45 MPa and maximum value obtained at 15% CNs was 57.30 MPa. In 2016 Ye et al. [29] prepared PVA based film reinforced with eucalyptus lignosulfonate calcium (HLS) particles. Different HLS to PVA (0/100, 5/95, 5.85, 25/75, 35/65, 50/50 and 60/40 wt./wt.) were dissolved in 100 ml distil water stir at 95°C for 3 h and then dried it at 70°C at vacuum oven. Pure PVA have tensile strength of 48.4 MPa, elongation at break 220.7% and Young's modulus 707.9 MPa. With the addition of HLS (35%) tensile strength increased to 124.15% whereas Young's modulus increased to 57.19%. SEM image of pure PVA film is shown in Figure 3D. Nath et al. [30] fabricated PVA based composited reinforced with unmodified fly ash (FA) and modified with sodium lauryl sulfate (SLS). The addition of FA/SLS-FA to neat PVA result in increased in tensile strength of film by 74.8% and 33%, respectively. In 2008 Lu et al. [31] developed polyvinyl alcohol based composite in which microfibrillated cellulose was used

Table 1: Application of PVA polymer.

| Year | Material | Application | Field | Reference |
|------|---|---|--------------|---------------------------------|
| 1943 | Fluid prepared by glycerin, urea, sulfathiazole, methyl cellulose and PVA | Treatment for burns | Medical | Skinner and Waud [11] |
| 1944 | Sulfathiazole in PVA | Determine the rate and depth of diffusion of sulfathiazole into the underlying tissue | Medical | Waud [12] |
| 1949 | PVA film combined with ethylene dichloride | Positive-replica technique for electron microscopy which reproduces the contour variations of the specimen surface, and permits direct visual interpretation of elevation | Electronic | Schwartz et al. [13] |
| 1951 | PVA | Plombage material for thoracic surgery | Medical | Levine et al. [5] |
| 1951 | Cement and polyvinyl alcohol | Cement which shows low loss of water from the slurry | Civil | Ludwing Norman [14] |
| 1960 | PVA bag and epoxy resin | Fabricating hip disarticulation sockets | Medical | McLaurin and Hampton [15] |
| 1963 | Esterification of polyvinyl alcohol | Preparation of polyvinyl cinnamate by schotten-baumann reaction | Chemistry | Tsuda [16] |
| 1968 | PVA glues | Developing a universal method for taking and mounting stable soil monoliths | Soil science | Borowiec and Domzat [17] |
| 1979 | PVA and polyacrylamide films with polymer-Cu ²⁺ complexes | Semiconducting cul surface layers | Electronic | Fukuda and Kuze [6] |
| 1979 | PVA | Crust strength of silty soils | Soil science | Page [18] |
| 1986 | Water and PVA | Development of hydrogel and its medical application | Medical | Tamura et al. [7] |
| 1990 | Polydepsipeptide dissolved chloroform/dichloroacetic acid pouring into PVA solution | Polydepsipeptide microspheres for drug delivery systems | Medical | Yoshida et al. [19] |
| 1994 | PVA with dimethyl sulfoxide | Highly swollen polymer gel actuator | Medical | Hirai et al. [20] |
| 2003 | Bifunctional aldehydes and PVA | Improving paper wet/paper sheet strength | Medical | Xu et al. [8], Kamelet al. [21] |
| 2005 | PVA and epichlorohydrin | Swollen PVA gel | Medical | Li et al. [22] |
| 2011 | PVA/polyaniline thin films | Supercapacitor application | Electronic | Patil et al. [9] |
| 2015 | Chitosan/PVA films | Time temperature indicator to indirectly indicate food quality changes | | Stefani et al. [10] |

as a reinforcement material. To prepared film 5 wt.% PVA solution with water was stirring at 95°C for 2 h and after cooling to room temperature microfibrillated cellulose (1, 5, 10 and 15 wt.%) was added. Mechanical testing of PVA based film is done. The Young's modulus and tensile strength increased with increasing the MFC content up to 10 wt.% and then tends to level off at higher MFC content. At 10 wt.% MFC content, Young's modulus of the composite film increases by 40%. Ching et al. [28] fabricated and characterized of polyvinyl alcohol (PVA) based composite reinforced with nanocellulose and nanosilica using film casting technique and concluded that 3 wt.% of nanocellulose optimized the tensile strength and tensile modulus of the composite. Further addition of nanosilica remarkably improved the tensile strength and tensile modulus of PVA composite which can be detected by thermomechanical properties. Table 2 represent mechanical properties of different PVA based composites/films in details.

2.1.1 PVA based biocomposite

Due to sustainability and environment impact issue attention toward environmentally friendly and complete degradability has been shifted. From past 10 to 12 years developments of biodegradable material have been increased. Figure 2 represents the procedure for obtaining PVA based composite/film. PVA is completely biodegradable and widely used for synthesis of biomaterials. Qiu and Netravali [37] fabricated microfibrillated cellulose (MFC)/PVA biodegradable composite at different content (5%, 10%, 15%, 20%, 30%, 40% and 50% by wt). The effect of crosslinking with glyoxal was also studied. It was found that neat PVA has fracture strength 34.1 MPa while strength goes on increasing with increase in the percentage of MFC upto 40% with the strength of 89.9 MPa. Figure 3B represents the SEM image of fracture surface of MC-PVA composite. Abdulkhani et al. [38] prepared cellulose/PVA biocomposite film which is pretreated with 1-n-butyl-3-methylimidazolium chloride. It was found that cellulosic film shows higher tensile strength as compared with cellulose/PVA film. In 2011 Zhang et al. [36] prepared PVA/cellulose biocomposite before mixing the cellulose fiber subjected to pan-milling to break intra- and inter-molecular hydrogen bonds. The tensile result shows that with the increase in number of cycle of pan-milling the strength is increased and maximum value obtained at 40 pan-milling cycles i.e. 16.4 ± 0.2 MPa. Marvdashti et al. [44] improved the physicochemical properties of Alyssum homolocarpum seed gum (AHSG) films using polyvinyl alcohol (PVA).

FTIR and SEM results showed the formation of hydrogen bonds or other interactions between the OH group of PVA and the OH and carboxyl groups of AHSG, forms a uniform and homogeneous network and improves the mechanical strength of the blend films with high PVA. These results indicated that PVA/AHSG blend films had good compatibility. With the increase in AHSG percentage in blend films, the ductility of the film is decreased. Table 2 represent mechanical properties of different PVA based composites/films in details.

2.1.2 PVA based films

Due to vast application of PVA such as in food industry, packaging industry and medical field development of PVA based blend films and membrane had been done such as, Sudhamani et al. [33] fabricated homopolymer films based on gellan and PVA at the different ratio. Tensile strength results show that strength for pure and blend vary between 3.5 and 5.6 MPa and decreases with increasing the PVA amount. In 2003 Srinivasa et al. [32] prepared chitosan-PVA blend films with ratio (100–0, 80–20, 60–40, 40–60, 20–80, 0–100%ratio, w/v). Mechanical testing shows that higher content of chitosan shows higher tensile strength with minimum elongation. Limpan et al. [45] fabricated myofibrillar protein (FMP)/PVA blend bio-films with different FMP/PVA (10:0, 8:2, 6:4, 5:5, 4:6, 2:8, 0:10) ratio and effect of pH level (3 and 11) also studied. It was found that with the increase in the percentage of PVA tensile strength increases and vice versa for the case of FMP. The blend films with pH level 3 have higher strength in case of higher PVA percentage whereas for higher FMP percentage pH level 11 blend films show higher strength. Another application PVA in preservation dehydration of ethylene glycol had been studied by Hyder and Chen [35]. They prepared chitosan-polyvinyl alcohol (CS-PVA) blend membrane which was crosslinked with trimesoyl chloride (TMC)/hexane. Five weight percentage solution of PVA with DI water and 1 wt.% solution with acetic acid was mixed in ratios of CS–PVA: 25–75, 50–50, 70–30, 75–25, 80–20 and crosslinking was done by dipping the membrane into 0.5 wt./vol.% TMC/hexane. It was found that tensile strength of crosslinked CS-PVA films were higher in films which had the higher percentage of CS and maximum value obtained for CS–PVA (80–20) ratio was 74.5 ± 2.7 . Application of PVA in food packaging industry had been studied by Kanatt et al. [48] they prepared chitosan (Ch) and PVA films by mixing the PVA and Ch solutions at various ratio (1:1, 1:2 and 2:1) with Glycerol (0.1% v/v) as plasticizer and mint extract (ME)/

Table 2: Mechanical properties of PVA based composites.

| Year | Composite/nanocomposite/biocomposite | Mechanical properties | | | Reference |
|------|---|---------------------------|--------------------------|----------------|--------------------------|
| | | Tensile strength (MPa) | Elastic modulus (GPa) | Elongation (%) | |
| 2003 | Chitosan-PVA (100–0) | 55.56±4.65 | 1.874±0.342 | 8±2.56 | Srinivasa et al. [32] |
| | Chitosan-PVA (80–20) | 46.99±3.85 | 1.528±0.248 | 26.84±7.87 | |
| | Chitosan-PVA (60–40) | 31.95±6.2 | 0.539±0.099 | 28.9±11.7 | |
| | Chitosan-PVA (40–60) | 37.23±3.82 | 0.345±0.105 | 60.58±9.01 | |
| | Chitosan-PVA (20–80) | 32±5.65 | 0.231±0.072 | 70.55±6.9 | |
| | Chitosan-PVA (0–100) | 25.64±3.86 | 0.12±0.056 | 105.47±6.87 | |
| 2003 | Gallen-PVA (ratio 3:1, 3:2, 1:1, 2:3 and 1:3) | 3.5–5.6 | – | – | Sudhamani et al. [33] |
| 2006 | PbS/PVA (0, 2.3 and 4.6 mass% of PbS) | 46.8±1.5 | 0.465±0.13 | 225±50 | Kuljanin et al. [34] |
| | | 51.6±1.9 | 0.645±0.105 | 257±50 | |
| | | 53±3.1 | 0.73±0.145 | 267±32 | |
| 2009 | CS | 65.1±1.9 | – | 8.15±0.9 | Hyder and Chen [35] |
| | PVA | 57.9±2.1 | – | 11.2±0.8 | |
| | CS-PVA1 | 67.9±2.8 | – | 11.5±1.1 | |
| | CS-PVA2 | 70.4±2.5 | – | 10.1±1.2 | |
| | CS-PVA3 | 74.7±2.1 | – | 8.3±0.9 | |
| | CS-PVA4 | 74.1±2.3 | – | 8.5±0.8 | |
| | CS-PVA5 | 74.5±2.7 | – | 8.2±0.9 | |
| 2010 | PVA/nano cellulose linen (20%, 40% and 60%) | – | – | 26.8–108.53 | Ibrahim et al. [27] |
| | PVA/nano cellulose cotton linter (20%, 40% and 60%) | – | – | 16.58–88.74 | |
| 2011 | PVA | 14±0.5 | 0.0447 | 339.3±0 | Zhang et al. [36] |
| | PVA/cellulose-1 | 8.8±0.6 | 0.0963 | 76.3±7.2 | |
| | PVA/cellulose-5 | 9.3±0.2 | 0.0905 | 118.2±6.2 | |
| | PVA/cellulose-10 | 10.5±0.6 | 0.0782 | 225.9±20.7 | |
| | PVA/cellulose-20 | 11.6±0.8 | 0.0703 | 222.2±22.1 | |
| | PVA/cellulose-30 | 13.3±1 | 0.0684 | 278.3±15 | |
| | PVA/cellulose-40 | 16.4±0.2 | 0.0554 | 374.4±6.4 | |
| 2012 | PVA | – | 0.248±0.023 | – | Qiu and Netravali [37] |
| | Crosslinked PVA | – | 0.666±0.009 | – | |
| | MFC-PVA (10 wt. MFC content) | – | 1.033±0.007 | – | |
| | Crosslinked MFC-PVA (10 wt. MFC content) | – | 1.404±0.009 | – | |
| 2013 | Cellulosic film | 129.7 | 0.1297 | 24.7 | Abdulkhani et al. [38] |
| | Cellulose/PVA film | 104.9 | 0.0469 | 30.6 | |
| 2013 | PVA | 57.02 | – | 391.47 | Xu et al. [39] |
| | PVA/CNs | 75.2 | – | 340.61 | |
| | PVA/CNs/AgNPs-0.36 | 74.39 | – | 342.66 | |
| | PVA/CNs/AgNPs-1.77 | 81.21 | – | 230.71 | |
| | PVA/CNs/AgNPs-3.47 | 72.48 | – | 259.88 | |
| | PVA/CNs/AgNPs-6.71 | 64.67 | – | 315.66 | |
| 2015 | Neat PVA | – | 2.75 | 57% | Guzman-Puyol et al. [25] |
| | PVA-TFA | – | 0.025 | 693% | |
| 2016 | PVA | 25.3±3 | 2.32±0.3 | 149±7 | Kashyap et al. [40] |
| | PVA-GO | 63±5 | 5.82±0.6 | 170±5 | |
| | PVA-rGO | 39±5 | 2.55±0.3 | 208±4 | |
| | PVA-H | 23±3 | 1.73±0.5 | 147±5 | |
| 2016 | CS-PVA (50–50) blend | 8 | 0.0001 | 17.16 | Jahan et al. [41] |
| | 0.1 g KNO ₃ | 10.09 | 0.86 | 21.67 | |
| | 0.2 g KNO ₃ | 18.9 | 0.057 | 26.8 | |
| | 0.3 g KNO ₃ | 19.18 | 0.432 | 31.9 | |
| | 0.4 g KNO ₃ | 20.23 | 0.126 | 34.57 | |
| | 0.5 g KNO ₃ | 31.9 | 0.0245 | 67 | |
| 2016 | PVA | 44±1.5 | 1.4±0.1 | 112.5±8.6 | Sonker et al. [24] |
| | TH-CL-PVA | 121.6±5.9 | 7±0.2 | 2.9±0.9 | |
| | GA-CL-PVA | 66.3±2.5 | 2.4±0.1 | 134.5±8.5 | |
| | WANT-PVA | 55.5±1.5 | 3.2±0.1 | 99.3±6.4 | |

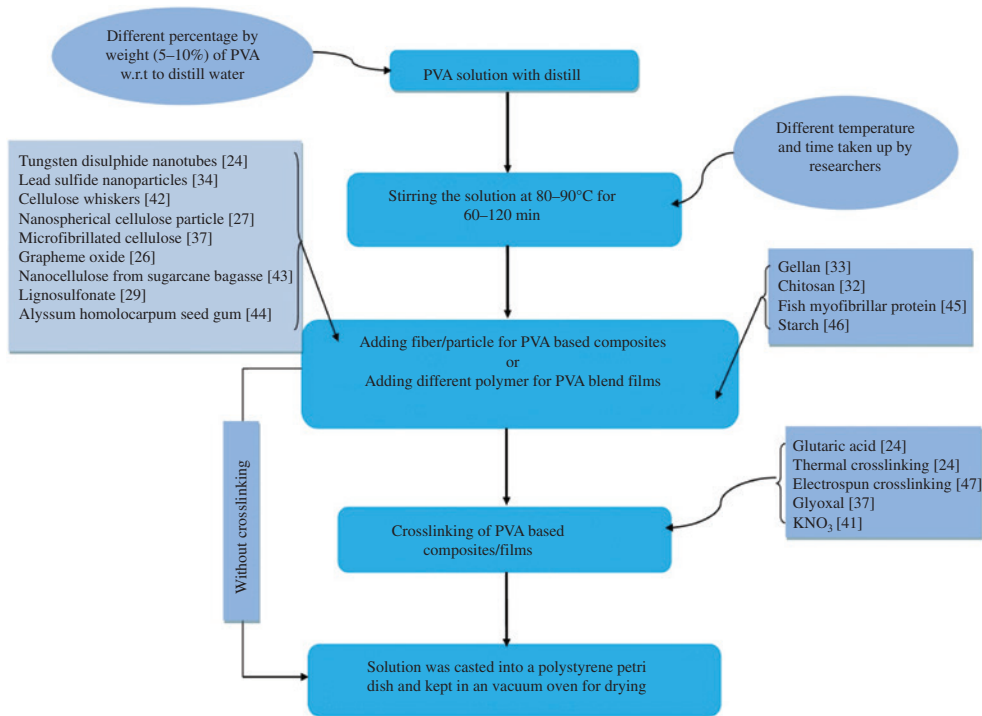


Figure 2: Preparation of PVA based composites/films.

pomegranate peel extract (PE) was added at concentration of 0.1%. The result shows that films which had higher PVA concentration had high tensile strength. The addition of ME/PE results in the increase of tensile strength with maximum value 41.07 ± 0.88 MPa for C1P2P (1:2 Ch:PVA ratio and 0.1% PE). Tian et al. [46] fabricated polyvinyl alcohol/starch blend films by melt processing and investigated the effect of composition and humidity. FTIR spectra result indicated that the OH groups on starch and PVA formed hydrogen bonding interactions, which could improve the compatibility of the two components. The tensile strength, elongation at break and Young's modulus decreased with increasing content of starch. However, at 50% starch content, the flexibility of the blend films was still high, with the elongation at break more than 1000% and tensile strength of 9 MPa, which was superior to the commonly LDPE package films. Therefore, these kinds of blend films exhibited wide application potentials as packaging materials. Jahan et al. [41] studied the effect of ionic crosslinkage with KNO_3 on chitosan-PVA blend film to enhance the mechanical strength and percentage elongation. The result shows that tensile strength of the CS-PVA (50/50) blend was increased by 298.75% and percentage of elongation from 7.16% to 67% after crosslinking with KNO_3 (0.5 g). Table 2 represent mechanical properties of different PVA based composites/films in details.

2.1.3 PVA based nanocomposite

From past few years research has been shifted toward nanocomposite [49] because of high compatibility result in improvement in mechanical properties (modulus, strength etc.), decrease in water absorption etc. Kashyap et al. [40] developed graphene oxide (GO) reinforced PVA nanocomposite. The result shows that tensile strength of neat PVA film was 25.3 ± 3 MPa whereas PVA-GO had 63 ± 5 MPa and Young's modulus of PVA film is 2.32 ± 0.3 MPa whereas PVA-GO had 5.82 ± 0.6 MPa. Li et al. [50] fabricated PVA/cellulose nanowhiskers/chitosan nanocomposite. One weight percentage CNWs and PVA (5%) were added at different percentage of chitosan. Result shows that PVA/chitosan (chitosan 15 wt.%) composites had a much lower elongation at break than pure PVA whereas PVA/CNWs nanocomposite films showed an increase in both tensile strength and elongation at break as compared with pure PVA films due to increased interactions between PVA chains and CNWs via hydrogen bonding. Mandal and Chakrabarty [43] prepared PVA and nanocellulose (2.5, 5, 7.5 and 10 wt.% w.r.t. solid PVA content) from sugarcane bagasse based nanocomposite. For crosslinking glyoxal (10 wt.% of solid PVA) was used. Figure 3C represent the SEM image of surface of NC-PVA (5 wt.% of NC) composite. The tensile strength of neat PVA and crosslinked

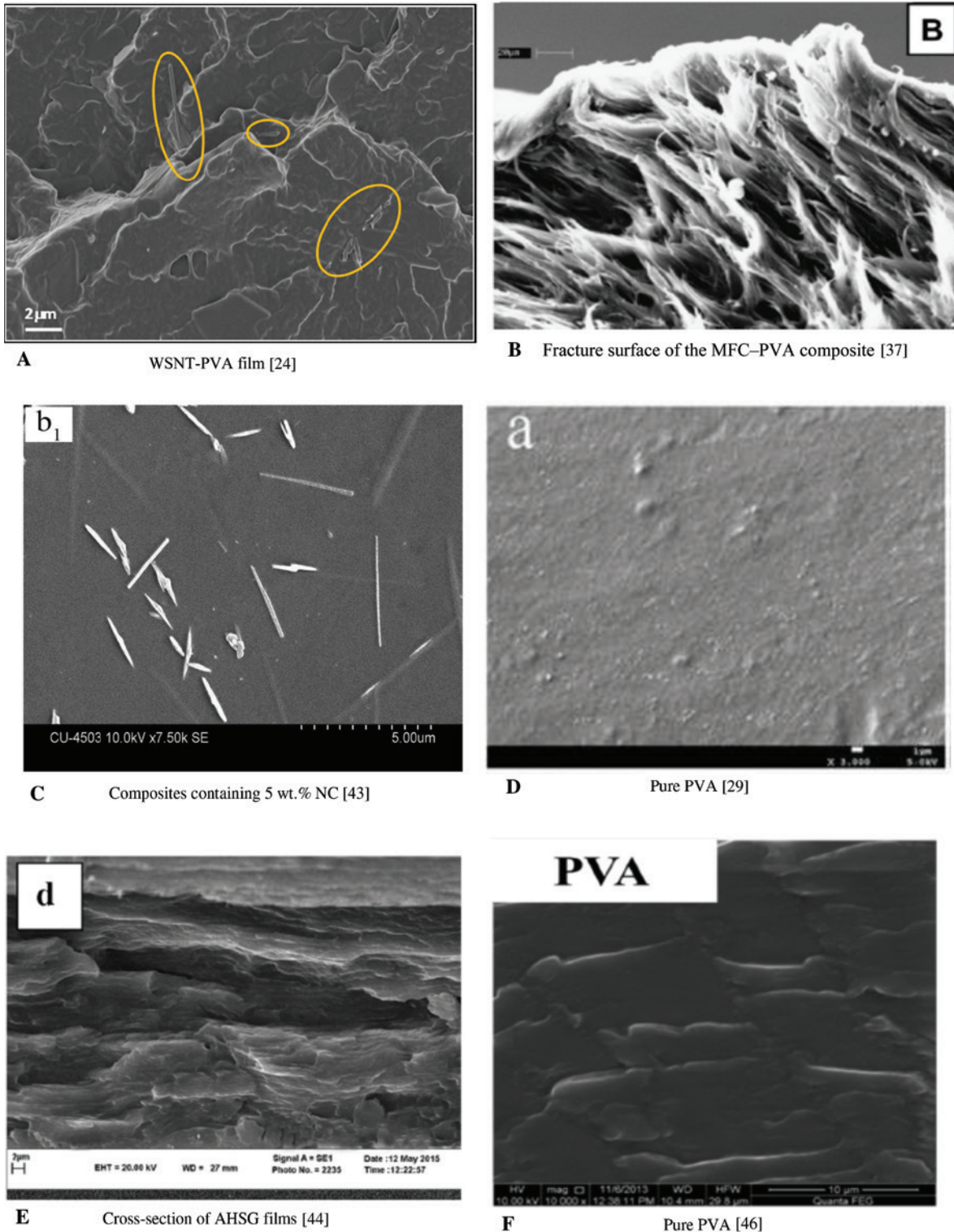


Figure 3: SEM image of PVA based composite/film. (A) WSNT-PVA film [24]. (B) Fracture surface of the MFC-PVA composite [37]. (C) Composites containing 5 wt.% NC [43]. (D) Pure PVA [29]. (E) Cross-section of AHSG films [44]. (F) Pure PVA [46].

PVA films were 41.3 kPa and 57.7 kPa, respectively. There was an approximately 48% improvement in the tensile strength of the PVA nanocomposite films with the

addition of nanocellulose at 7.5 wt.%. In case of crosslinking maximum strength was achieved at 5 wt.% nanocellulose content which was higher by 44% with respect to

cross linking PVA film. Xu et al. [39] prepared nanocomposite based on PVA/cellulose nanocrystals/silver nanoparticle. The 10% PVA solution in 100 ml distilled water was mixed with a specific amount of aqueous CNs and CNs/AgNPs to obtained different composition. Neat PVA had tensile strength of 57.02 MPa and maximum tensile strength obtained for PVA/CNs/AgNPs-1.77 was 81.21 MPa. Yang et al. [47] fabricated PVA film through electrospinning with malic anhydride (MA) as a cross linker. Five to ten percentage PVA solutions with DI water were prepared stirred at 80°C for 2 h, sulfuric acid was added to maintain pH value 2–3 and then MA (PVA/MA = 30/1, 21/1, 20/1, 19/1 and 10/1, mole/mole) was added then solution electrospun immediately. The prepared membrane was boiled in water for 1 h. Study of dissolved mass loss was studied and found that PVA/MA (20/1) show minimum mass percentage. Roohani et al. [42] prepared nanocomposite based on PVA which was reinforced with cellulose whiskers (0, 3, 6, 9 and 12 wt.% for PVA) prepared from cotton linter. The tensile strength of nanocomposites were studied under different relative humidity and it was found that there was increased in tensile modulus of nanocomposite films when whisker content was been increased for each relative humidity condition. For given filler content, there was a significant decrease of the tensile modulus with increasing the humidity. Kuljanin et al. [34] used lead sulfide (PbS) nanoparticle (4.6 and 2.3 mass%) and PVA to fabricates nanocomposite by colloidal chemistry methods. Tensile results show that with the increase in PbS content

breaking strength increases and the maximum value of 53.0 ± 3.1 MPa for 4.6% PbS was obtained. Table 2 represent mechanical properties of different PVA based composites/films in details.

2.2 Water absorption properties of PVA based composites/films

Presence of –OH (hydroxyl groups) in PVA result in high water up take, swelling and solubility in water which is one of the disadvantage of PVA film/composite. Due to water absorption the mechanical strength of the PVA film/composite decreases. But in some cases such as packaging of hot food product high water vapor permeability is required which come under advantages for PVA. Works have been done to reduce the water up take properties of PVA film/composite through crosslinking and adding other additive such as to reduce water up take thermal crosslinking by heating the PVA film at 125°C (0.5–12 h) and glutaric acid crosslinking [24] with 30 wt.% (compare to PVA) is done by. It was found that TH-CL-PVA had 69.7% and GA-CL-PVA had 24.9% of swelling as compare to PVA which had 152.8% of swelling. Study of PVA for DMFC cell had been done by Helen et al. [51] by fabricating membrane based on cesium salt of heteropoly acid, zirconium phosphate and polyvinyl alcohol. To prepare the film zirconium phosphate (10 wt.%) and Orthophosphoric acid (30 wt.%) added to 10 wt.% PVA solution with water and

Table 3: Swelling, water uptake and solubility of different composite/film.

| Year | Composite/film | Swelling (%) | Water up takes (%) | Solubility (%) | Reference |
|------|---|--------------|--------------------|----------------|------------------------|
| 2006 | PVA-ZrP-C _s ₁ SWA | 100 | 260 | – | Helen et al. [51] |
| | PVA-ZrP-C _s ₂ SWA | 85 | 140 | – | |
| 2012 | PVA | 105.6 ± 5.5 | – | – | Qui and Netravali [37] |
| | Crosslinked PVA | 78.3 ± 2.7 | – | – | |
| | Crosslinked MFC-PVA | 75.1 ± 8.8 | – | – | |
| 2013 | Cellulosic film | – | 33–42% | – | Abdulkhani et al. [38] |
| | Cellulose/PVA film | – | 73–78% | – | |
| 2016 | PVA | 132.8 ± 8.9 | – | – | Sonker et al. [24] |
| | TH-CL-PVA | 69.7 ± 2.6 | – | – | |
| | GA-CL-PVA | 24.9 ± 2.6 | – | – | |
| | WSNT-PVA | 155.3 ± 3.6 | – | – | |
| | WSNT-TH-CL-PVA | 73.1 ± 2.8 | – | – | |
| | WSNT-GA-CL-PVA | 26.8 ± 4.2 | – | – | |
| 2017 | PVA:AHSG (100:0) | – | – | 75 ± 3.5 | Marvdashti et al. [44] |
| | PVA:AHSG (80:20) | – | – | 66 ± 3 | |
| | PVA:AHSG (60:40) | – | – | 41 ± 2.5 | |
| | PVA:AHSG (50:50) | – | – | 34 ± 2.1 | |
| | PVA:AHSG (40:60) | – | – | 32 ± 1.8 | |
| | PVA:AHSG (80:20) | – | – | 15 ± 2.8 | |
| | PVA:AHSG (0:100) | – | – | 13 ± 1.3 | |

stirring the solution at 343 K for 8 h. Water absorption test was performed on PVA based membrane by immersed it into deionized water for 2 h there is about 240% water uptake for PVA-ZrP-Cs₁-SWA hybrid membrane and 140% water uptake for PVA-ZrP-Cs₂-SWA hybrid membrane. Effect of crosslinking (crosslinking was done by dipping the membrane into 0.5 wt./vol.% TMC/hexane) on swelling degree was study and result show that swelling degree varies from 68 to 76% and films having the higher percentage of PVA shows higher swelling degree. The effect of glyoxal crosslinking on swelling power of composite had been studied which shows that swelling power decreases with crosslinking from 105.6% to 78.3% from neat PVA to crosslinking PVA and swelling power of crosslinking MFC-PVA was 75.1%. Abdulkhani et al. [38] studied water absorption properties which ranged from 33% to 42% for cellulosic film and from 73% to 78% for cellulose/PVA film which shows that due to the presence of -OH water absorption of cellulose/PVA film is higher than cellulosic film. Tian et al. [46] studied the effect of starch on water up take of PVA/starch blend film. With the increase of starch, the degree of crystallinity of PVA component decreased and water uptake at equilibrium decreased. With the increase of RH, the water uptake at equilibrium of the resulting blends increased. Figure 3F represent SEM image of pure PVA film. Srinivasa et al. [32] study water solubility of the blend film results show that neat PVA is completely soluble in water whereas the solubility of a film decreases with increase in the percentage of FMA in blend films. Films with pH level 11 show higher solubility as compared with pH level 3 films. Marvdashti et al. [44] studied the effect of Alyssum homolcarpum seed gum (AHSG) on the solubility of PVA/AHSG film. Figure 3E represent the SEM image of cross section of ASHG film. It was found that with the increase in AHSG percentage the solubility of the film in water decreases. PVA film had 75 ± 3.5% solubility as compare to AHSG film which had 13 ± 1.3% solubility. Table 3 represents water uptake, solubility and swelling properties of different PVA based composites/films in details.

3 Conclusions

This paper provides an overview on mechanical and water absorption properties of PVA based composites/films. Preparation of PVA based composites/films with fiber/particle reinforcing by different researchers have been review and it was found that PVA composites/films were mechanically stronger and tougher than the PVA films due to better interfacial adhesion. Properties of modified

films/composites depend on the methods of modification, crosslinking and different blending polymer. To reduce water absorption crosslinking were done by many researchers have been discussed. Research is in progress to overcome the limitations such as cost effective, water absorption and biodegradability of PVA based composites/films, to have it is widespread application in different field.

References

- [1] Sazanov YN. *Russ. J. Appl. Chem.* 2001, 74, 1253–1269.
- [2] Long R. *The Production of Polymer and Plastics Intermediates from Petroleum*, Plenum Press: New York, 1967.
- [3] Finch CA. *Poly(vinyl alcohol): Developments*, John Wiley and Sons: London, 1992.
- [4] Sakurada I. *Polyvinyl Alcohol Fibers*, Marcel Dekker: New York, 1985.
- [5] Levine S, Grow JB, Hurst A, Perlmutter HM. *Chest Journal* 1951, 20, 126–133.
- [6] Sumita O, Fukuda A, Kuze E. *J. Appl. Polym. Sci.* 1979, 23, 2279–2291.
- [7] Tamura K, Ike O, Hitomi S, Isobe J, Shimizu Y, Nambu M. *Trans. Am. Soc. Artif. Intern. Organs* 1986, 32, 605–608.
- [8] Xu GG, Yang CQ, Deng Y. *J. Appl. Polym. Sci.* 2004, 93, 1673–1680.
- [9] Patil DS, Shaikh JS, Dalavi DS, Kalagi SS, Patil PS. *Mater. Chem. Phys.* 2011, 128, 449–455.
- [10] Pereira Jr., VA, de Arruda INQ, Stefani R. *Food Hydrocoll.* 2015, 43, 180–188.
- [11] Skinner G, Waud RA. *Can. Med. Assoc. J.* 1943, 48, 13–18.
- [12] Waud RA. *Can. Med. Assoc. J.* 1944, 51, 229–234.
- [13] Schwartz CM, Austin AE, Weber PM. *J. Appl. Phys.* 1949, 20, 202.
- [14] Ludwig Norman C. Low-water-loss cement, U.S patent US2576955 A Dec. 4, 1951.
- [15] McLaurin CA, Hampton FL. *Orthotics and Prosthetics* 1960, 14, 40–42.
- [16] Tsuda M. Schotten-baumann esterification of poly(vinyl alcohol). I., From Government Chemical Industrial Research Institute, Tokyo, Hiratsuka, Kanagawa, Japan (1963).
- [17] Borowiec J, Domżał H. The possibilities of using polyvinyl acetate in taking and mounting soil monoliths, *Roczniki Gleboznawcze, T. Xix, Dodatek, Warszawa* (1968).
- [18] Page ER. *J. Soil Sci.* 1979, 30, 643–651.
- [19] Yoshida M, Asano M, Kumakura M, Katakai R, Mashimo T, Yuasa H, Imai K, Yamanaka H. *Colloid. Polym. Sci.* 1990, 268, 726–730.
- [20] Hirai T, Nemoto H, Hirai M, Hayashi S. *J. Appl. Polym. Sci.* 1994, 53, 79–84.
- [21] Kamel S, El-Sakhawy M, Nada AMA. *Thermochim. Acta* 2004, 421, 81–85.
- [22] Li W, Xue F, Cheng R. *Polymer* 2005, 46, 12026–12031.
- [23] Kiro A, Bajpai J, Bajpai AK. *J. Mech. Behav. Biomed. Mater.* 2016, 65, 281–294.
- [24] Sonker K, Wagner HD, Bajpai R, Tenne R, Sui XM. *Compos. Sci. Technol.* 2016, 127, 47–53.

- [25] Guzman-Puyol S, Ceseracciu L, Heredia-Guerrero JA, Anyfantis GC, Cingolani R, Athanassiou A, Bayer IS. *Chem. Eng. J.* 2015, 277, 242–251.
- [26] Li Y, Umer R, Samad YA, Zheng L, Liao K. *Carbon* 2013, 5, 321–327.
- [27] Ibrahim MM, El-Zawawy WK, Nassar MA. *Carbohydr. Polym.* 2010, 79, 694–699.
- [28] Ching YC, Rahman A, Ching KY, Sukiman NL, Chuah CH. *BioResources* 2015, 10, 2264–2277.
- [29] Ye DZ, Jiang L, Hu XQ, Zhang MH, Zhang X. *Int. J. Biol. Macromol.* 2016, 83, 209–215.
- [30] Nath DCD, Bandyopadhyay S, Gupta S, Yua A, Blackburn D, White C. *Appl. Surf. Sci.* 2010, 256, 2759–2763.
- [31] Lu J, Wang T, Drzal LT. *Compos. Part A* 2008, 39, 738–746.
- [32] Srinivasa PC, Ramesh MN, Kumar KR, Tharanathan RN. *Carbohydr. Polym.* 2003, 53, 431–438.
- [33] Sudhamani SR, Prasad MS, Sankar KU. *Food Hydrocoll.* 2003, 17, 245–250.
- [34] Kuljanin J, Omor MIC, Djokovic V, Nedeljkovic JM. *Mater. Chem. Phys.* 2006, 95, 67–71.
- [35] Hyder MN, Chen P. *J. Membr. Sci.* 2009, 340, 171–180.
- [36] Zhang W, Yang X, Li C, Liang M, Lu C, Deng Y. *Carbohydr. Polym.* 2011, 83, 257–263.
- [37] Qiu K, Netravali AN. *Compos. Sci. Technol.* 2012, 72, 1588–1594.
- [38] Abdulkhani A, Marvast EH, Ashori A, Hamzeh Y, Karimi AN. *Int. J. Biol. Macromol.* 2013, 62, 379–386.
- [39] Xu X, Yang YQ, Xing YY, Yang JF, Wang SF. *Carbohydr. Polym.* 2013, 98, 1573–1577.
- [40] Kashyap S, Pratihar SK, Behera SK. *J. Alloys Compd.* 2016, 684, 254–260.
- [41] Jahan F, Mathad RD, Farheen S. *Mater. Today: Proc.* 2016, 3, 3689–3696.
- [42] Roohani M, Habibi Y, Belgacem NM, Ebrahim G, Karimi AN, Dufresn A. *Eur. Polym. J.* 2008, 44, 2489–2498.
- [43] Mandal A, Chakrabarty D. *J. Ind. Eng. Chem.* 2014, 20, 462–473.
- [44] Marvdashti LM, Koocheki A, Yavarmanesh M. *Carbohydr. Polym.* 2017, 155, 280–293.
- [45] Limpan N, Prodpran T, Benjakul S, Prasarnpran S. *J. Food Eng.* 2010, 100, 85–92.
- [46] Tian H, Yan J, Rajulu AV, Xiang A, Luo X. *Int. J. Biol. Macromol.* 2017, 96, 518–523.
- [47] Yang E, Qin X, Wang S. *Mater. Lett.* 2008, 62, 3555–3557.
- [48] Kanatt SR, Rao MS, Chawla SP, Sharma A. *Food Hydrocoll.* 2012, 29, 290–297.
- [49] Chaabouni O, Boufi S. *Carbohydr. Polym.* 2017, 156, 64–70.
- [50] Li HZ, Chen SC, Wang YZ. *Compos. Sci. Technol.* 2015, 115, 60–65.
- [51] Helen M, Viswanathan B, Murthy SS. *J. Power Sources* 2006, 163, 433–439.