

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/



CrossMark

Spinning Techniques of Poly (vinyl Alcohol) Fibers for Various Textile Applications

Shamous M. Ibrahim ^a, Ayman El said ^a, Tamer Hamouda ^{b*}

^a Textile department, Faculty of Applied Arts, Helwan University, Egypt. ^b Textile Research and Technology Institute, National Research Centre

Abstract

Polyvinyl alcohol is a water-soluble and biodegradable polymer. PVA is also considered an environmentally friendly material, which made PVA one of the most synthetic polymers used in many industrial applications. This review identifies PVA in terms of its properties and the different methods of spinning PVA fibers to be used in textile applications. There are different spinning methods that are used in production of PVA fibers such as wet spinning, melt spinning, gel spinning, and dry-wet spinning. In addition to some modification that may be carried out to improve the properties of PVA fibers such as esterification, etherification or acetalization of hydroxyl groups. Also, Blending PVA fibers with other natural and synthetic fibers such as conton, wool, tencel, viscose, acrylic, and polyester to acquire a textile fiber provides superior properties to the final yarns such as comfort, thermal properties, air permeability, and water absorption. PVA blended fibers were produced with different techniques namely core yarns (hollow center yarns), blended yarns (microporous yarns) and doubled yarns (reduced twist yarns). Each technique present different properties to the resulting yarn. PVA is classified as non-hydrolysable known as high-performance fiber and partially hydrolysable and hydrolysable. The applications in which PVA was used are many and varied. Whereby PVA utilized in manufacturing the environmental friendly packaging. Also, PVA is used in textiles industry to form a protective layer namely for warp sizing, which works to reduce yarn breakage during the weaving process. The biomedicine application is also one of the most important applications that tended to benefit from polyvinyl alcohol.

Key words: Polyvinyl alcohol, Wet spinning, Dry Spinning, Melt Spinning ;

1. Introduction

Polyvinyl alcohol (PVA) is a water-soluble synthetic polymer [1-2]. PVA polymer is a polyhydroxy and characterized by its high chemical polymer resistance, good mechanical and physical properties, and complete biodegradation in presence of suitable microorganisms, which led to its use in different industrial applications [3]. PVA is available in the market in different degrees based on viscosity and degree of hydrolysis [4-6]. Nevertheless, PVA is considered an inert substance [7], some chemical modifications are applied to PVA to improve its reactivity. The hydroxyl groups in the PVA allows for chemical modifications. These modifications are esterification, etherification or acetalization of hydroxyl groups [8-9]. In 1939 Sakurada and Yazawa have worked on production of water insoluble PVA fibers by using heat treatment and formalization and the final fibers were produced by wet spinning technique [10]. The Biodegradability of PVA can be improve by blending PVA with starch (ST), as ST is considered a biodegradable polymer in soil and organic fertilizer [11]. PVA Polymer can be found in three different forms namely; fully hydrolyzed (98% or higher), partially hydrolyzed (typically between 87% - 89% hydrolyzed), and intermediate (89% - 98% hydrolysis) [12-13].

The state of PVA hydrolysis or partial hydrolysis of polyvinyl acetate affects the physical properties of PVA. Whereby, PVA is classified into partially hydrolyzed and fully hydrolyzed. PVA is produced with different molecular weights ranging from (20,000

^{*}Corresponding author e-mail: <u>tehamoud@ncsu.edu</u>.

Receive Date: 17 May 2023, Revise Date: 09 July 2023, Accept Date: 10 July 2023 DOI: 10.21608/EJCHEM.2023.211636.7983

^{©2024} National Information and Documentation Center (NIDOC)

to 400,000), solubility, flexibility, tensile strength, and adhesion. As, all these properties depend on the length of the initial vinyl acetate polymer and the degree of hydrolysis under alkaline or acidic conditions. To identify PVA, there are several characteristics that distinguish it, such as pH, viscosity, drying loss, melting point, refractive index, heavy metals, and residues on ignition [14]. Effect of different parameters on PVA nanofibers mechanical and structural parameters investigated to be used in different applications [15]. PVA nanofibers been developed for different applications such as a reinforcement to enhancing the mechanical properties of cementitious composite and for nonwoven composite material to enhance the sound absorbency [16-17].

On the other hand, the advantages of high Young's modulus, strong adhesion, good dispersion, and low fiber price are achieved in high-performance polyvinyl alcohol (PVA) fibers [18]. By optimizing the spinning solution, the orientation of the polymer chains, and the drafting parameters, an improvement in the tensile mechanical properties of the fibers can be obtained [19]. To prepare new materials with improved properties, trend to the technique of modifying organic polymers. It was found that the hydroxyl groups present in PVA achieve easy modification of PVA polymers [9].

1.1 Polymeric Textile Fibers

Fiber is a substance that has no restrictions in its chemical composition. Fiber may exist in different forms such as: metallic, mineral, or organic. However, non-metallic fibers are polymers, either natural or synthetic. Fibers can be classified into natural fibers such as: cotton, wool, and silk. And synthetic fibers such as: polyvinyl alcohol and polyethylene, etc. Figure 1 shows the polymers classification in textile fibers.

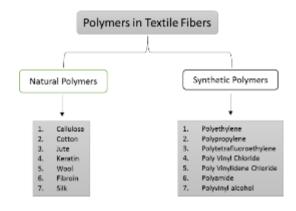


Fig.1 Polymers in textile fibers

1.2 Properties of PVA Polymer

It was found that the greater the molecular mass of PVA the greater the tensile strength, crystallinity, and adhesion ability. On the other hand, the flexibility decreases, and its viscosity becomes high and the specific gravity changes from 1.19 to 1.31. It was found that by changing the forms of hydrogen bonding, the crystal structure of PVA changes [4] [20]. Depending on the number of hydroxyl groups present in the PVA polymer, its physical, mechanical, and chemical properties are affected. PVA is not manufactured by polymerization of its structural monomer (vinyl alcohol) because of its unstable nature for commercial production of PVA [4]. The current trend relies on compounding, mixing and modification in developing new polymeric materials rather than relying on chemical synthesis only. Due to the advantages of PVA such as the non-toxicity, biocompatibility, high water content and ease of processing, the PVA polymer is an ideal polymer for use in various applications such as textile products, flexible devices in electronics, optoelectronics, and bioengineering. It is also important for modifying some properties of PVA to open the field for use in other applications [4].

There is more than one chemical method for modifying the PVA polymer. They can be divided into commonly used methods and modern methods, and both methods depend on the hydroxyl groups on the backbone [1]. The common method is such as acetylation, carbamation, etherification, or esterification of hydroxyl groups. The new method trend is such as click chemistry. Whereas, it opens the way for PVA to be used in other applications such as molecular sensing, biological and biomedical, membrane fuel cells, chemical sensors, adsorption of toxic metal and optoelectronic devices [4] [21]. When manufacturing polymeric nanocomposites, the uniform dispersion that occurs of the nano-fillers in the polymer matrix is problematic. The uniform dispersion plays an important role in the manufacture of multifunctional compounds. Compounding can be achieved by mixing different materials, which can be divided into two parts, either polymer-additives or polymer-polymer. Melt compounding, in situ polymerization, and solution blending are the common compounding techniques [22]. PVA is characterized by the fact that it contains many hydroxyl groups linked to the carbon chain of PVA, which allows it to combine with other materials through hydrogen bond [4].

1.3 Polyvinyl Alcohol Spinning Process

Spinning is a process by which fibers are manufactured from polymers, as it is done using a spinneret to produce multiple continuous filaments. Fibers are manufactured from a large number of different polymers. Through solution spinning the polyvinyl alcohol fibers are produced. There is more than one type of spinning process that can be used to produce PVA fibers such as wet spinning, dry spinning, and air-gap wet spinning [23][10]. Although, the production of PVA by melt spinning technique is difficult, there are several attempts and research have been done to produce PVA fibers by melt spinning by using a plasticizer [24].

1.3.1. Wet Spinning

1.3.1.1 Wet spinning with sodium sulfate coagulation bath.

Wet spinning process is used to produce staple fiber and tow. In ordinary wet spinning, the PVA dissolves in water in concentration of 14-16% under heating condition. In order to avoid gel formation, the spinning solution must be kept above 70 °C. Then filtration and deaeration take place. Hence, comes the next step, which is the extrusion of the spinning solution through spinnerets into a coagulation bath containing a saturated solution of sodium sulphate at 40-50°C. When comparing the coagulation speed of PVA with viscose, it was found that the coagulation speed of PVA is slower and requires a longer time in the coagulation bath comparing to Viscose production [32].

Utilization of vertical spinning machine carry many advantages, whereas the coagulation process go smoothly and also reduce required floor space [33]. In this process, the fibers are drawn in a second heated coagulation bath and then dried. The produced fiber is soluble in hot water. To overcome this, the fibers are subjected to a drawing process and thermal treatment in hot air or by using hot rollers at 210-240 °C. However, it must be taken into consideration that the temperature of the heat treatment process is higher than the temperature of the drawing process. In order to stabilize the fiber structure during heat treatment, a small shrinkage is allowed. As a result of exposing the fibers to heat treatment, crystallization of the polymer chains occurs in the fibers, so the solubility of the fibers in hot water decreases. The process of acetalization takes place on heat treated fibers, where the fibers are passing through an aqueous solution containing1-5% formaldehyde,10-20% sulfuric acid, and 5–20% sodium sulfate for 10-60 at 5080°C min to reach a degree of formalization of 25-35 mol% [32].

The acetalization process is affected by several factors such as reaction conditions, the conditions of the drawing processes, and the heat treatment applied to the fibers. As a result of acetalization process, the resistance of the fibers to hot water increases. Moreover, the mechanical and chemical properties of the fibers change. In the case of staple fiber production, mechanical crimping and cutting occur to heat-treated tow and then the cut fiber is formalized. For industrial application suitability, the formalized tow must be directly subjected to a stretch-break spinning system to convert it into spun yarns. The produced threads have high strength and toughness [34].

1.3.1.2 Wet spinning with alkaline coagulation bath.

In the case of the fibers produced by the wet spinning method with sodium sulfate coagulation bath, transparent fibers with high tensile strength can't be obtained. The cross-section of the fibers is in the form of a cocoon and the skin/core has a heterogeneous structure. This is due to the coagulation proceeding with the rapid dehydration from the outside of the extruded jet of the spinning dope.

But the PVA fibers produced form PVA dope that are spun in an aqueous solution of concentrated alkali have a circular cross-section, a homogeneous and compact structure. The produced fibers from this method are transparent and have several advantages represented in the possibility of being drawn at a high degree, which give improved tensile strength and modulus in addition to better water resistance. In this method when PVA dope comes in contact with an alkaline coagulant it become gel immediately as the dehydration continue homogeneously [35]. Japanese companies are using this method. As the alkaline substance used in the coagulation bath is sodium hydroxide at a concentration 200 g/l and at a temperature of 40-50 °C. To obtain a highly drawn fiber with a higher modulus, modifications have been made by using an aqueous acid spinning dope that contains a small amount of boric acid. Initially, the purpose of developing this method was to obtain a high-tenacity, high-modulus yarns to be used in the tire cord application. But then the PVA yarn is modified to obtain high-modulus fibers to be used as a substitute for asbestos fibers in reinforcing cement, as this fiber has a tenacity of 12 cN/dtex and a modulus of 274 cN/dtex [32].

1.3.1.3 Wet spinning with organic solvent.

When comparing polyvinyl alcohol with polyethylene in terms of coefficient of crystalline, polyvinyl alcohol is the one that has a higher crystalline modulus. In this method, organic solvent is used as the PVA solution passes through several stages. First, the hot diluted PVA solution is slowly cooled in the polyol, and then the highly crystalline PVA precipitates. This phenomenon has been associated with gel-spinning and ultrahigh-drawing procedures. As the gel fibers formed from the PVA solution in glycerine, have a high degree of polymerization up to 38000, .The resulting fiber is drawn at high temperatures, which results in fibers that have a high tenacity of up to17 cn/dtex and a modulus of 555 cn/dtex [32].

1.3.2 Melt Spinning

Melt spinning is one of the methods of spinning, as it is considered one of the simplest spinning types, as this type of spinning is highly efficient and environmentally friendly [36]. Whereas, this method depends on continuous steady state elongational flow of processing. As, first, the molten polymer is extruded, and then exposed to cooling, which results in solidification. It is also possible to obtain high mechanical properties of the fibers by stretching and annealing the fibers. Often, these processes take place during the melt spinning process either into air or through an air gap into a cold-water bath [25].

Early studies on PVA fiber spinning reported that it is difficult to use melt spinning to produce PVA fibers, and this is due to the multi-hydroxyl structure of PVA [36]. Whereas, melting point so close to its decomposition temperature. Therefore, PVA fibers were produced for a while by means of gel spinning [37], crosslinking wet spinning [38] and alcoholysis spinning from polyvinyl acetate [39]. But all these methods depend mainly on wet spinning, which contains complex such as dissolution, steps coagulation bath or spinning bath and desolventization, etc. It also needs to high molecular weight PVA [36].

Many studies have been done for possibility of producing PVA fibers by melt spinning through blending, copolymerization and plasticization [40]. However, these methods remained limited in use due to the complex treatment of PVA [36]. A study reported that an environmentally friendly technology was adopted to try to reduce the melting point of PVA, achieve heat treatment, and control the ultra-molecular structure of PVA [41]. The resulting fibers from this melt spinning process are characterized by circular cross, uniform structure, and excellent drawing ability [42]. There are studies to plasticize PVA polymers by using pseudo ionic liquids (PILS), which are known as green solvents, in addition to glycerin (GL). This method was developed to produce PVA fibers by melt spinning for the first time, in addition to improving the heat treatment ability of PVA polymers. It was found in the plasticizing system (PILS/GL) that cation (OH), the anion (Cl), and the hydrogen form a strong hydrogen bonds with the hydroxyl groups of PVA [43]. When comparing plasticized PVA polymer with pure PVA, the result shows that the melting point of the plasticized PVA is lower, wider thermal processing and better melt fluidity than the pure PVA. The study also recorded a successful production of PVA fibers by melt spinning using the GL/ChCI-GL system. Produced PLA fiber characterized by smooth surface with diameter of 116 µm and circular cross section. Mechanical testing of the produced plasticized PLA fiber shows increase in tensile strength with value of 1208 MPa compare with 357 MPa for pure PVA and Young's modulus with value of 23 GPa compare with

6.10 GPa for pure PVA [43].

Another research was conducting on studying the crystallization behavior of PVA fibers produced by melt spinning during hot drawing. The results indicate that during drawing the PVA fibers crystallize in three stages: initial stage, the stage of crystallization induced by stress, and the stage of slowly increasing. It can be found from the study that there is a direct relationship between fiber crystallization and drawing temperature. Thus, the temperature of the draw increased, the crystallization of PVA fibers increased. But the behavior is different when the drawing speed increasing. Whereas, the crystallinity of PVA fibers increased at first with increasing the drawing speed and then decreased [36]. The study also indicated that the drawing process is an essential process for the production of high-strength, high-modulus fibers. As, the crystallization that occurs as a result of stress during the drawing process is considered one of the most important phenomena. During the drawing process, crystallization of the polymer and

crystallization rate increased which improve the mechanical properties of polymer products [36].

A study on PVA, investigated the effect of heat during drawing on the crystallization of PVA fibers. The result indicated that the higher the draw temperature, the higher the crystallization of the PVA fibers under the same drawing ratio. This is due to the fact that PVA chains are subject to expansion along the direction of tensile stress when the temperature increases during drawing, in which cause an increase in the crystallization rate and crystallinity of PVA fibers [36]. Although, in the recent years, the focus was on the produced compounds from PVA loaded with carbon nanotubes [44-45]. It was found that both gel spinning and electrospinning [46] are methods for producing PVA fibers reinforced with CNT [47]. But wet spinning is the most used technique for different types of composite fibers. Studies have shown that producing composite fibers from PVA/CNT by both wet and gel spinning is less effective and more complex due to the difficulty in dispersing CNT particles [48].

The study succeeded in proving that it is possible to produce composite fibers from Polyvinyl Alcohol and Multi-Walled Carbon Nanotube (PVA/MWCNT) by Melt Spinning. This is achieved through the dispersion of CNT in the composite plasticizer, swollen melt spinning, and post-treatment. Two methods were conducted to investigate the effect of structure development on the produced composite PVA/MWCNT fiber. First, using dispersing agent such as Tween 80 and second is cold and hot drawing to improve the mechanical properties of PVA composite fibers. Which results in an increase in the degree of crystallization of PVA and the degree of orientation. It also improves the alignment of nanotubes along the fiber axis [48]. There is also a study that succeeded in to benefit from carbon

nanotubes (CNT) and polyvinyl alcohol (PVA) in the production of composite fibers (CNT//PVA) through the melt spinning process [48]. Fig. shows that production of PVA fibers by melt spinning. Whereas, PVA/MWCNT composite fibers were produced by dispersing CNT in composite plasticizers and using melt spinning, and after spinning, treatments are carried out [48].

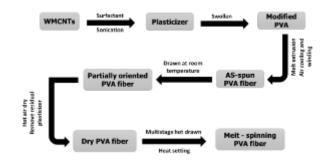


Fig. 7 Steps for producing PVA fibers by melt spinning.

The results of this study show that the mechanical properties of the PVA/CNT composites depend largely on the crystallinity of the polymer and the degree of orientation. As the PVA polymer used in this study was a partially crystalline polymer [48]. Interest in plasticizers has begun in recent years due to their ability to form a new hydrogen bond interaction with the hydroxyl groups of PVA, in addition to destroying inter-/intra- hydrogen bonding [49-50]. Studies have shown that water is one of the best solvents for PVA as it is known as a green solvent. One of the drawbacks of using water as a solvent is its low boiling point. As, the water evaporate rabidly which affect the spinnability of the PVA fibers. Therefore, the use of co-plasticizer with water such as caprolactam (CPL) helps to form a hydrogen bond interaction with the PVA chains and helps to keep them inside the PVA fibers without extraction treatment. Therefore, the study adopted the use of water/caprolactam (W/ CPL) as plasticizing system for the production of PVA fibers

by melt spinning. Whereas, this system increases the boiling point of water. The results of spinning PVA/W/CPL showed decrease in melting point and produced fibers exhibit a circular and uniform structure. These results open the door of utilization of PVA in cement applications [50].

One of the studies indicated to the use of Janus particles with hybrid kaolinite in melt spinning system. Whereas the particles settle in the PP-PVA interface, and the polymer compatibility enhanced significantly. The results of the study were as follows: the mechanical properties of the produced PP/PVA (70/30) filaments were improved, as the Young's modulus increased significantly. The results also showed that the samples containing KJ exhibit a low melt flow index, and with the addition of kaolinite particles, the crystallization rate of PP decreased [51].

Fig. shows that the stress-strain curves of the filaments without/with kaolinite particles and before and after selective extraction. Using KL particles cause poor mechanical properties, where the tenacity and breaking elongation decrease. On the other hand, Young's modulus remains stable. But when using 1% wt of KJ particles a slight decrease in both tenacity and breaking elongation occurred. Meanwhile, the value of Young's modulus increased slightly. Experience also proves that when using 5 wt % of KJ an increase in the value of Young's modulus occurs by a larger percentage (from 1417 ± 136 MPa for unfilled blends toward 2227 ± 370 MPa), with a sharp 57% more. On the other hand, the elongation at break decreases and tenacity is slightly enhanced [51].

This study prove that the use of the Janus particle significantly enhances the Young's modulus of the fibers and also strengthen the interface as a result of the special localization of the kaolin particles. In addition to a decrease in break elongation as a result of the interfacial localization of the fillings. Hence, this study proves that it is possible to treat the weak effect on the mechanical properties of melted fibers by using modified particles from Janus in the fields of melt spinning technology [51]. As proven by a study that partially hydrolyzed PVA has a lower molecular interaction than fully hydrolyzed PVA. Therefore, partially hydrolyzed polyvinyl alcohol (PVA) was used to prepare thermoplastic polyvinyl alcohol (TPVA), which leads to improve the flowability in addition to higher water solubility. The used PVA in this study has a saponification degree of 86 mol% and three different degrees of polymerization of 800, 500, and 300 are used. On the other hand, Glycols are used as plasticizers for PVA. Whereas, glycols consist of an alcohol with two hydroxyl groups on adjacent carbon atoms. One of the most suitable glycol plasticizers is glycerin, as it is characterized by its high compatibility with PVA, in addition to its high thermal stability [24]. The produced polymers are called thermoplastic polyvinyl alcohol (TPVA). The results of this study showed that the water solubility of TPVA is affected by the degree of polymerization, hydrolysis and spinning conditions. Whereas, the increases of the spinning temperature cause longer time for the fiber to dissolve. This attribute to the improvement of crystallinity via the thermal treatment which also cause difficulties on drawing with adequately retained water solubility. On the other hand, the fiber sample with high spin speed or hot drawing did not show a significant increase in dissolution time. The study used partially hydrolyzed PVA to prepare TPVA [24].

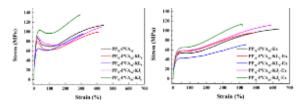


Fig. 8 stress-strain curves of the filaments without/with kaolinite particles and before and after selective extraction

Another study investigated the use of 40% by weight of water to plasticize the PVA powder and then stored the plasticized PVA powders in an airtight container, which results in a complete seep of water into the PVA. Results indicated that the higher the drawing ratios, the higher the degree of crystallinity and the melting point of the profiled PVA fibers. An improvement occurred in both the crystal structure and orientation. The study also proved that good control of the relaxation of the molecular chain during the hot drawing results in a variation in the cross-sectional shape of the profiled PVA fibers less than 10%, which assures excellent profile retention. The result reveled that an eight-time draw ratio, the tensile strength of the triangular, cruciform, trilobal and wavy fibers were 585, 559, 481, and 585 MPa respectively. Producing a novel fiber that are usable for composite reinforcement [52] were obtained. Fig. show SEM images of profiled as spun PVA fibers with different cross-sectional shapes [52].

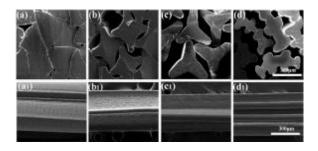


Fig. 9 Sem images of profiled as spun PVA fibers with different cross-sectional shapes (a) triangular, (b) cruciform, (c), trilobal, and (d) wavy [52]

Another study provided evidence of the possibility of using polyvinyl alcohol fibers with a triangular crosssection prepared by melt spinning, to reinforce the epoxy resins. As the result of a complex between particles and plastics, PVA fibers with a triangular cross-section were produced through melt spinning and hot drawing [53]. The results revealed that that triangle fibers have a high specific surface area which makes them suitable for the reinforcement of epoxy resin. As, the contact area increases with the epoxy matrix. In the Epoxy matrix, the fibers were fixed better, which resulted in improving the mechanical properties of the composites. The tensile performance of triangular PVA fiber/EP composites is also improved. The results of this study demonstrated the successful preparation of triangular epoxy composites reinforced with PVA fibers [53].

Another study investigates the effect of degrees of hydrolysis (HD) and molecular weights of polyvinyl alcohol on the thermal and mechanical properties and crystallinity of (PLA/PVA) blended yarns. The results of the thermogravimetric analysis (TGA) indicated that the PLA/PVA mixture containing PVA with higher molecular weights (MW) and degrees of hydrolysis (HD) exhibit a better thermal stability. The results showed that using low amounts of PVA (3% by weight) did not affect the tensile strength of the PLA/PVA blends irrespective to the degree of hydrolysis and molecular weight. However, it was found that with increasing the amount of PVA, the tensile strength decreased, especially for mixtures containing 20% by weight of PVA, with 98% of degrees of hydrolysis (HD) [54].

1.3.3 Gel Spinning

Gel spinning process is one of the common methods for PVA fibers production. One study investigated the possibility of producing PVA fibers by incorporating Cellulose whiskers (CW) prepared from native cotton into PVA as reinforced fillers (PVA/CWs) through gel spinning. The results showed a high degree of orientation of CW along the axis of the prepared fibers. Due to the presence of surface sulphate groups of CWs, the PVA molecules are converted into a catalytic polyene structure. Which results in the disappearance of the dynamic cooling crystallization peak after PVA melting, as indicated by the DSC test results. Scanning electron microscope (SEM) images of the as-spun neat PVA and PVA-CW30% fibers showed that all the fibers have smooth surfaces and even diameters. These results proved that it is possible to use CWs up to 30% by weight for reinforcing PVA polymers without negatively affecting the spinnability of PVA fibers during or on the final appearance of the fibers. Fig. shows SEM images of spun fibers of neat PVA, and PVA-CW30% fibers. This study succeeded in proving the possibility of using CWs to reinforce crystalline polymers such as PVA to produce a fiber known as PVA-CW. This is due to some reasons which are good dispersion of CWs in PVA solution, high uniaxial orientation of CWs in PVA matrix and finally positive interaction and stress transfer between PVA with oriented CWs [55].

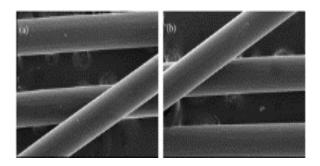


Fig. 10 SEM image of spun fibers: (a) neat PVA, and (b) PVA-CW30% fibers

Another study showed the possibility of producing thermally stable PVA fibers by gel spinning of high molecular weight (HMW) PVA by using dimethyl sulfoxide/water (8/2, v/v) as a solvent and boric acid as a cross-linking (B/PVA). This study compared the structure and properties of B/PVA fibers and HMW PVA fibers obtained by the same spinning technique without crosslinking (NB/PVA) [56]. The results indicated that using boric acid (0.3% by weight) as a cross-linker and zone drawing resulted in a significant change in the properties of HMW PVA gel fibers. Where it led to an improvement in the thermal properties of PVA fibers. On the other hand, and in case of PVA fibers cross-linked with boric acid (BA/PVA), the X-ray diffractogram result showed a peak shift to lower angle of the original PVA unit cell. The study also reported that with a draw ratio of 15 the tensile strength and Young's modulus of (BA/PVA) fibers were 23.1 and 308.3 g/d, respectively [56].

Another study investigated the production of high strength composite fibers of PVA reinforced with graphene oxide (rGO). Solvothermal reduced reduction of graphene oxide (GO) in a solution of PVA/dimethyl sulfoxide (DMSO)/H2O was carried out to acquire a macroscopically homogeneous dispersion of (PVA/rGO). Then, by using gel spinning followed by hot drawing, (PVA/rGO) composite fibers were obtained. Results showed that when (rGO) was combined by 0.1% by weight with PVA to produce composite fibers the mechanical properties of the fibers improved, and the tensile strength increased for pure PVA fibers from 1.8 GPa to reach 2.2 GPa for composite fibers PVA/rGO. Whereas, an increase in tensile strength and Young's modulus by 20.6% and 20.8%, respectively. The results also indicated a relatively strong interfacial interactions between (rGO) nanosheets and PVA which caused improving in the thermal stability of composite fibers. The higher the amount of rGO used the greater the thermal stability. From the foregoing, it can be concluded that the incorporation of rGO into PVA is a successful method for producing high performance PVA fibers [57].

Another study utilized gel spinning in the production of a composite fiber known as PVA/lignin. Due to the compatibility of PVA with lignin. The use of a coagulation bath containing methanol/acetone with high percentage of acetone, resulted in drawable, maintaining the lignin within the fibers and increasing the melting point of the gel. The resulting fibers had better mechanical performance with an average tensile strength of 1.1 GPa, Young's modulus of 37 GPa, and a toughness of 17 J/g. Structural analysis showed a highest crystallization index for PVA. When conducting infrared spectroscopy of the fibers, hydrogen bonding was found between lignin and PVA. Also, it was found that lignin/PVA fibers can resist solubility in boiling water, unlike pure PVA fibers. The results also indicated that the higher the amount of lignin the greater the swelling of the fibers [58].

Another study showed the possibility of producing polyvinyl alcohol PVA/attapulgite (ATT) composite fibers using gel spinning. The results indicated that the structures and properties of PVA/ATT nanofibers are affected by the amount of ATT. The results structures and properties examination conducted by chemical and physical analysis of a group of PVA/ATT nanocomposite fibers indicated that the amount of ATT has a significant effect on the structures and properties of PVA/ATT nanofibers. Whereas, when ATT content increased from zero to 3% by weight the melting temperatures, crystals, initial decomposition temperatures, and the maximum decomposition temperatures of the PVA/ATT nanofibers increased. On the other hand, the results alternated when ATT contents increased from 5% to 7% by weight [59]. Another study investigated the utilization of short cellulose nanofibers (SCNF) in reinforcing polyvinyl alcohol (PVA) fibers. In the experiment, different percentages of SCNF were added to the PVA solution, which was then spun by gel spinning. The results showed that the lower the percentage of SCNF in the PVA fibers the greater the direction of the PVA crystallization. On the contrary, when the percentage of SCNF is increased above 2 or 3% the result is a network formation of filtered SCNFs that prevents alignment. This study proved that the tensile strength and Young's modulus of PVA/SCNF fibers with short cellulose nanofibers with a weight ratio of approximately 6 are 60 and 220%, respectively which is higher than pure PVA. It was also found that the combination of wet drawing during gel spinning and drawing after heating at a high temperature after drying influenced the molecular orientation of PVA [60].

One study provided evidence that the best solvent for spinning doping and coagulant is a mixture of DMSO/HO = 80/20 (w/w) and methanol to obtain PVA fibers with the highest drawability. As a result of the ability of the DMSO/H2O mixture to promote gel formation, the produced PVA fibers have a high drawability. The result indicated that when the undrawn gel fibers subjected to hot two-stage drawing under conditions with maximum drawability, highest strength and Young's modulus PVA fibers were obtained. In addition, when reducing the coagulation temperature of 6 wt% of the dope, a higher draw ratio of PVA fibers were obtained. The results were also revealed that when preparing the spinning dope from PVA with a DP of 5000 and a mixed solvent DMSO/H₂O (80/20), the produced fibers showed a highest tensile strength of 2.8 GPa and the highest Young's modulus of 64 GPa [61].

1.3.4 Dry-Wet Spinning

One of the ways to produce PVA fibers is dry spinning. Whereas, PVA fibers can be obtained by spinning a concentrated aqueous solution of PVA from the spinneret to air [10] [62]. There are two types of dry spinning, namely low draft spinning and high drafts spinning [32]. In low-draft spinning, the PVA solution is prepared with concentration of 40-45% with draft ratio approximately one. But in high draft spinning, the used polymer concentration is 20-40% and the draft ratio is from one to several tens [10]. In this type of spinning, PVA powder and water are mixed and then converted into granules that can be spun .Then, there is a melting of the granules in the extruder, and the solution is filtered, deaerated and transferred to a spinneret. The final step is to harden the fibers by the exposure to hot air, and then transfer the fiber to the drying machine, where the fibers are dried and taken by the winder. Studies have shown that the speed of dry spinning ranges from 300-600 m/min while wet spinning speed is lower at approximately 50 m/min. Thus, dry spinning is higher than that of wet spinning [10].

1.3.4.1 Low- Draft Spinning

Low-draft spinning is using aqueous spinning dope with concentration ranges between 41-45% and very high viscosity. This spinning process is carried out by dissolving the PVA granules in the presence of water by heating them in an extruder under pressure. The spinning of highly viscosity spinning dope process can be carried out at a temperature of 130-160 °C in air at Ca. 50 °C. The fiber draw ratio depends on the spinning dope extrusion rate of the spinneret as the cooled and solidified filament is wound with a low draw ratio of 0.3-1.0. (Draft ratio = winding rate/extrusion rate). During the drying process the temperature is raised gradually, and the drying occurs gradually. The final dried filament exhibits a circular cross section, homogeneous structure, and low strain. Fibers can be drawn to the highest drawing rate with a temperature close to the melting point. This type of spinning process produces fibers that have sufficient resistance to hot water. In addition, produced yarns by this method can be heavier and suitable for industrial applications. The aim of this method in the beginning was to produce monofilaments heavier than 110-1100 dtex, but it expanded to be used in the production of multiple filaments, such as 1330 dtex / 200 filament [32].

1.3.4.2 High-Draft Spinning

High-draft spinning is using aqueous spinning dope with concentration ranges between 28-41% at temperature of 90-95°C. The spinning takes place in a spinning tube consisting of a drawing zone at temperature ranged between 30-80°C, RH of 55-95%, and a drying zone temperature of at >80°C and RH <50%. Whereas, when the filaments are passing through the spinning tube, it subjected to a large drafted, dried, and taken off at a winding speed ranging from 200 to 500 m/min. Then the dried fibers are drawn on hot and heat treated, and it is sometimes possible moreover acetalized. This method can be used to obtain finer filaments for use in textile applications. A mixture of PVA and amino acetalized PVA is used to produce fibers that are used in clothing and can be dyed using acid dyes. The yarn produced by this method are water soluble. Commercially available water soluble PVA fibers are made by using PVA with low degrees of polymerization and saponification, and heat treatment conditions are controlled. In general, in dry spinning, the polymer solutions are extruded through a spinneret and then exposed to a hot air stream t evaporates the solvent and leaves the polymer fibers [32].

One of the studies was able to prove the success of the possibility of using dry-wet spinning in the production of PVA fibers with high strength and high Young's modulus using a self-designed spinning equipment (Figure 11). The results revealed that PVA fibers have one crystalline type, and this was shown by measuring XRD, and the thermal resistance of PVA fibers was better than that of PVA, and this was indicated by the results of the thermogravimetric analysis (TGA) and that the fibers produced by this method have high strength and it is sufficient to meet the requirements of civil and architectural engineering use. Whereas, the average tensile strength and Young's modulus of PVA fiber are 1.73 GPa and 40.02 GPa, respectively [18].

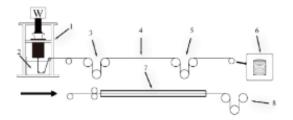


Fig. 11 Self-designed spinning equipment (1-extruder;2-coagulation bath;3,5,8-roller;4-stretching in air;6-extraction;7-stretching in heat pipe)

Another study indicated the possibility of producing PVA fibers by wet dry gel spinning by using dimethyl sulfoxide (DMSO) as a solvent and methanol as a cooling medium. The result indicated that the viscosity level is equalized for both solution that has a lower amount of PVA at a lower temperature and the solution that has a higher amount of PVA at a higher temperature. Also results revealed that the solution with a lower amount of PVA loses DMSO at a lower rate and this is due to the weaker gel capacity and the potential phase separation during coagulation In addition, the solution bounds more DMSO when the solution is closer to the gel point, which results in a difficult DMSO exchange process. Moreover, the study proved that the lower the amount of PVA in the solution, the stronger the fibers and the more appropriate crystallization and crosslinking will occur [63].

One of the studies investigated the possibility of producing PVA fibers by dry-wet spinning with crosslinking of boric acid (BA) known as PVA/BA fibers, in addition to using the mixed solvent of dimethyl sulfoxide (DMSO) and water to improve the

indicated that the higher the amount of BA the higher the degree of crosslinking of BA with PVA. The scanning electron microscopy indicated that the final fibers (PVA/BA) are characterized by smooth surfaces and decreasing in the fiber diameter at the beginning and followed by an increased after increasing the amount of (BA). Moreover, the mechanical properties of the fibers were measured and the results showed that the cross-linking is existed at an ideal BA content of 0.3% by weight and PVA/BA (0.3%) fibers have a highest tensile strength of 13.1 ± 0.4 cN/dtex and a highest Young's modulus of 360.2 ± 10.4 cN/dtex [64]. This study also produced PVA/BA fibers with different amounts of BA of zero and from 0.1 to 0.4 wt%. The results of Fourier transform infrared spectra (FTIR) analysis showed that the final yarn exhibit an increase in the degree of crosslinking between PVA and BA as the amount of BA increased. On other hand DSC, TGA, and XRD analysis showed increase in melting temperatures, thermal properties, and crystallinity at first followed by decreasing as the amount of BA increased [64].

mechanical properties of PVA fibers. Fourier

transform infrared spectra (FTIR) analysis results

Another study investigated the interlocking structure of PVA fibers during the dry-jet wet spinning process. The swelling DSC method was used to investigate the changes in the entanglement of PVA fibers during the spinning process. A swelling agent was used for PVA, which is a mixture of (DMSO) as a good solvent and (EG) as a weak solvent. It was found that disentangle of the entanglement structure of the PVA fibers occurred after the destruction of the crystalline phase in the swelling agent during heating. So, there are several factors affecting the interlocking of PVA fibers represented in spinning dope concentration, jet expansion ratio, extrusion shear stress and pull ratio for the whole spinning process. Reducing entanglement between chains of macromolecules

during the spinning process is essential to the possibility of producing high-performance fibers. As a finding in this study, as the draw ratio, degree of orientation, and crystallinity of the fibers are increased. Thus, the entanglement structure of PVA fibers can be reduced by controlling the overall spinning process. Therefore, the possibility of obtaining PVA fibers with a tensile strength of 17.5 cN/dtex can be achieved [65].

1.3.5 Mechanical Spinning of PVA Fibers

Textiles are used to meet human needs in various applications. Some textiles meet basic needs, such as clothing. On the other hand, the textiles that are produced for the purpose of meeting a specific requirement are known as technical textiles. The field of textile application has expanded because of the development of new fibers and processing methods [66]. To produce a product of two or more types of fibers, there are several methods namely, yarns spun, twist yarns, composite yarns, and blended yarns from different types of fibers. A product consisting of morethan one fiber is produced to utilize the advantages of each fiber that are blended in the yarn [67].

One of studies produced single jersey fabrics using conventional and hollow cotton yarns with different hollowness ratios. Thermal properties of the resulting fabrics were compared. Hollow yarns using a cotton/PVA core spun yarns was produced and then PVA was removed by washing [68]. After washing the PVA, the yarns to turn from core spun yarn to hollow yarns. After removing the PVA, the air permeability results showed increases compared to the fabric before washing. But when comparing the fabrics after washing with each other, the results show that the greater the core hollowness, the lower the air permeability of the fabric [68]. As a result, PVA fibers exhibit high thermal conductivity when compared with cotton fibers. Therefore, the results indicated that the higher the percentage of PVA in the core spun yarns, the higher the thermal conductivity of the fabric [68]. The thermal conductivity of the PVA core spun yarn fabrics were higher than that of the reference fabric and the thermal conductivity values increased with the increase in the PVA ratios in core spun yarns. This may be explained by the higher thermal conductivity values of PVA fibers than cotton fibers.

However, after washing the fabric, the results were alternated, as the sample that contained the highest percentage of PVA was the lowest in thermal conductivity, due to the removal of PVA, which has a high ability to heat conduction. Also, the greater the core hollowness, the greater the amount of air inside the yarn, so when compared to the control fabric, it was found that the control fabric has a higher capacity for thermal conductivity [68]. The thermal absorption of the fabrics after washing have decreased, and the results indicated that the thermal absorption of the hollow yarn fabrics was higher than that of the control fabric. The fabrics with the highest percentage of PVA had a high ability to absorb heat, so when touched for the first time, it gives a feeling of coldness [68]. The study also revealed that due to the removal of PVA fibers the water vapor permeability of the fabrics increased. Whereas, the water vapor permeability depends on two important factors namely the amount of air trapped in the yarn structure and the hollowness of the core in the hollow yarns.

Another study also dealt with the production of hollow yarns with fixed percentage of PVA in the core with the use of different raw materials in the sheath, namely cotton, viscose, and acrylic to produce jersey fabrics with permeable properties that allow their use in sports clothing. Control samples were produced 100% cotton, 100% acrylic and 100% viscose spun yarns [69]. The results indicated that after samples' washing the fabrics lost PVA fibers, and thus an increase in water vapor transmission occurred and the water vapor permeability of the fabrics also increased due to the trapping of air in the hollow yarns [69]. When compare control fabrics with fabric after removing PVA (hollow yarn fabric), it was found that all hollow yarn fabrics give better results in water vapor permeability [69].

Another study produced yarns using the technique of core sheath in which cotton, viscose, wool, and polyester raw materials were used in the sheath and PVA in the core. This study proved the possibility of producing yarns containing 50% less fibers with the same yarn diameter. However, hollow yarn's tenacity and elongation decreased with the increase in hollowness ratios, due to the removal of PVA [70].

The next part of the study utilized the produced hollow yarn before washing them in the production of knitted fabrics to investigate the effect of both the structure of the hollow yarns and the ratio of the core sheath of the hollow yarns on the permeability properties of the produced fabrics. Results indicated that before washing the fabrics there is a decrease in air permeability, no matter the type of fiber used in the sheath, due to the presence of PVA. But, after washing the fabrics and removing the PVA the results alternated, and the air permeability of the fabrics increased. Also, the water vapor permeability recorded an increase especially in the fibers in which the polyester material was used in the sheath [71]. The results indicated that when a comparison was made between the fabrics produced using 100% viscose and the fabrics produced using viscose/PVA (50%/50%) in terms of fluid conductivity, the fabrics produced with PVA showed the higher fluid conductivity. The study proved that regardless of the type of fiber used in the

sheath and after removing the PVA, there was a decrease in the bursting strength of the fabrics [71].

Another study aimed to produce a yarn with fine pores by washing treatment of blended yarn of PVA fiber and cotton fiber. The micro-pores were created by treating the blended fiber with hot water, which results in dissolving PVA fibers and pores creation. The study indicated the variables of the experiment that have influenced the properties of the yarns before and after washing were the percentage of PVA fibers, the yarn twist multiplier (TM) and the spindle speed [72]. The results showed that the blended yarn after washing, the yarn count became finer. It was also found that because of the shrinkage of the yarns during washing, there was a slight increase in twist per inch for all samples. Although after washing there are no significant changes in twist multiplier (TM). Also, the results showed that the higher the PVA content the lower yarn packing factor due to the presence of micro-pores in the yarn. On the contrary, at a low level of PVA and with an increase in spindle speed, an increase in the yarn packing factor occurs. A decrease in yarn tenacity also occurs for all samples after washing. On the other hand, the compressibility of the yarn after washing was increased due to PVA removal and to the appearance of fine pores inside the yarn structure [72].

There is another study that used a ply yarn of cotton and Tencel yarn with PVA as weft yarns to produce a woven fabric with comfort properties. Two-for-one twister technique was used to produce yarns that are used in the production of fabrics to achieve the characteristics of comfort for the user [73]. After washing the samples, the results indicated that when comparing the samples produced from Tencel ply yarn with those produced from single Tencel yarn, the air permeability is greater for the samples produced from Tencel ply yarn. This is due to the removal of PVA after washing and to the creation of open spaces between the fibers. Also, due to the presence of air inside the fibers after removing the PVA, the ply yarn has a lower thermal conductivity. There are two factors that affect the thermal absorption, which are the non-twist effect and the fiber material. It was found that the woven samples with a single yarn had a higher thermal absorption than the non-twisted fabrics. The results also indicated that the woven fabric made of untwisted weft yarns had a higher tensile strength than that produced yarn with single yarn [73].

Another study used micro-porous yarn and hollow yarn by using PVA fibers in the core for hollow yarns and as doubling yarn in micro-porous yarn to produce double face woven fabrics. The study also investigated the effect of these parameters on the values of air permeability and moisture transmission of the produced fabrics. The doubling yarn technique was used to produce the micro-pores yarn and the PVA as core was used to produce the hollow yarn with five different hole sizes [74]. The results revealed that the air permeability of the fabrics produced from hollow yarns is less than fabrics produced from micro-porous yarns and higher than the fabric produced from cotton yarns only. On the other hand, the difference in the percentage of porous yarns in the fabric did not show any effect on air permeability. When comparing the fabrics produced from cotton only with the fabrics produced from porous yarns, the results showed that the fabrics produced from porous yarns had a higher value for moisture transfer. However, in the case of fabrics produced from hollow yarns, it was found that the larger the hole size the larger the diameter of the yarn, which results in a decrease in the moisture transfer of the fabrics [74].

In one of the studies, two-component yarns are used which are cotton and PVA followed by dissolving PVA by exposure to hot water, so that hollow fabrics are produced [75]. The results indicated that the yarns that achieved the highest values of tenacity are the hollow, double, and blended yarns respectively. This is due to the presence of straight and continuous PVA yarns in the core in the case of core yarns, which achieves the highest effective spinning strength [75]. On the other hand, PVA yarns are in a spiral shape in the case of double pre hollow yarns leads to less yarn strength than that of core spun pre-hollow yarn. The results also showed that the yarns that achieved the least unevenness, thick places, thin places, and complete defects were doubled yarns, blended yarns and core yarns, respectively. Whereas, in the case of double yarns, the doubling process improves the evenness of the yarn. Core and double yarns did not show any difference in the level of neps. On the contrary, the blended yarns showed the lowest number of neps in the yarn [75]. Regarding the yarn hairiness, the results showed that the lowest index of hairiness recorded for core yarns, blended yarns, and double threads yarns respectively. As a result of using yarns with cotton fibers in the core yarns, it works to reduce the number of fibers in the cross-section of the yarn, and thus the number of fiber ends, which results in a decrease in hairiness in the yarns. However, in the case of blended yarns, it contains a greater number of fibers in cross-sections, and thus the number of fiber ends, which results in an increase in hair hairiness in the yarns. Despite that the number of fibers in the yarn cross-section are low in the doubled pre-hollow yarn, the results indicated an increase in hairiness in the doubled yarns compared to blended pre-hollow yarn. Which, due to the doubling processes, where the yarns are exposed to friction, which increases the level of hairiness [75].

2. Conclusion

Polyvinyl Alcohol (PVA) one of the most synthetic polymers used in different industrial applications. As

a result of PVA excellent properties such as watersoluble, biodegradable polymer, and environmentally friendly material. The current trend relies on compounding, mixing and modification in developing new polymeric materials rather than relying on chemical synthesis only. Several modifications are being made to PVA to open the field for use in other applications. Whereby, there is more than one chemical method for modifying the PVA polymer. There are different methods to produce PVA fibers, such as wet spinning, melt spinning, gel spinning, and dry-wet spinning. Therefore, the properties of the resulting yarn differ according to the production method. In the beginning, there was difficulty in producing PVA with melt spinning, but studies were conducted to investigate the possibility of using melt spinning in the presence of a plasticizer such as pseudo ionic liquids (PILS) and Glycerin (GL). In the wet spinning method, it is possible to change the coagulant bath solution such as sodium sulphate, alkaline, and organic solvent. There are two types of dry spinning, namely low draft spinning and high drafts spinning. In low-draft spinning, the PVA solution is prepared with concentration of 40-45% with draft ratio approximately one. But in high draft spinning, the used polymer concentration is 20-40% and the draft ratio is from one to several tens. Composite yarns that consist of PVA fiber with more than one material are produces by several methods namely, yarns spun, twist yarns, composite yarns, and blended yarns from different types of fibers. Yarn consisting of more than one fiber is produced to utilize the advantages of each fiber that are blended in the yarn. It is concluded from the foregoing that polyvinyl alcohol has a promising future because of its unique properties that differ according to the spinning method.

3. Declaration of conflicting interests

The Authors declare that there is no conflict of interest

4. Acknowledgements

The authors disclosed receipt of the following financial support for the research, authorship, and/or publication of this article: This work was supported by the Textile Alliance for deepen local manufacturing project funded by Academy of Scientific Research and Technology.

5. References

1. Awada , Houssein and Daneault, Claude. Chemical Modification of Poly(Vinyl Alcohol) in Water. Appl. Sci. 2015, Vol. 5, 4, pp. 840-850.

2. Ding, Bin, et al. Preparation and characterization of a nanoscale poly(vinylalcohol) fiber aggregate produced by an electrospinning method. Polymer Physics. 2002, Vol. 40, 13, pp. 1261-1268.

3. Chiellini, Emo, et al. Biodegradation of poly (vinyl alcohol) based materials. Progress in Polymer Science. 2002, Vol. 28, pp. 963–1014.

4. Aslam, Muhammad, Kalyar, Mazhar Ali and Raza, Zulfiqar Ali. Polyvinyl Alcohol: A Review of Research Status and Use of Polyvinyl Alcohol Based Nanocomposites. Polymer Engineering and Science. 2018, Vol. 58, 12, pp. 2119-2132.

5. Abdullah, Zainab Waheed , et al. PVA, PVA Blends, and Their Nanocomposites for Biodegradable Packaging Application. Polymer-Plastics Technology and Engineering. 2017, Vol. 56, 12, pp. 1307-1344.

6. Ye, Mao, Mohanty, Pravansu and Ghosh, Gargi. Morphology and properties of poly vinyl alcohol (PVA) scaffolds: Impact of process variables. Materials Science and Engineering:C. 2014, Vol. 42, pp. 289-294.

7. Thomas, Lynda V., et al. A biodegradable and biocompatible PVA–citric acid polyesterwith potential applications as matrix for vascular tissue engineering. J Mater Sci: Mater Med. 2007, Vol. 20, pp. 259–269.

8. Rescignano, N., et al. PVA bio-nanocomposites: A new take-off using cellulose nanocrystalsand PLGA nanoparticles. Carbohydrate Polymers. 2014, Vol. 99, pp. 47-58.

9. Gaina, Constantin, et al. Study on the Chemical Modification of Poly(VinylAlcohol) with 4-Maleimidophenyl Isocyanate. Polymer-Plastics Technology and Engineering. 2012, Vol. 51, 1, pp. 65-70.

10. Kim, H C. The structure of acrylic, polyvinylalcohol and polyvinylchloride fibers. [book auth.] S. Eichhorn, et al. Handbook of Textile Fibre Structure, Fundamentals and Manufactured Polymer Fibres. Cambridge : Woodhead Publishing, 2009.

11. Abdullah , Zainab Waheed and Dong , Yu. Biodegradable and Water Resistant Poly(vinyl) Alcohol (PVA)/Starch (ST)/Glycerol (GL)/Halloysite Nanotube (HNT) Nanocomposite Films for Sustainable Food Packaging. Frontiers in Materials. 2019, Vol. 6, pp. 1-17.

12. Morris, Barry A. Commonly Used Plastics and Substrates in Flexible Packaging. The Science and Technology of Flexible Packaging (Second Edition). United Kingdom : William Andrew Publishing, 2022, pp. 85-138.

13. Saad, Moulay. Review: Poly(vinyl alcohol) Functionalizations and Applications. Polymer-Plastics Technology and Engineering. 2015, Vol. 54, 12, pp. 1289-1319.

14. DeMerlis, C. C and Schoneker, D. R. Review of the oral toxicity of polyvinyl alcohol (PVA). Food and Chemical Toxicology. 2003, Vol. 41, 3, pp. 319-326.

15. Doustgani , Amir. Optimization of Mechanical and Structural Properties of PVA Nanofibers. Journal of Industrial Textile. 2016, Vol. 46, 3, pp. 901-913.

16. Pakravan, Hamid Reza, Latifi, Masoud and Jamshidi, Masoud. Ductility Improvement of Cementitious Composites Reinforced with Polyvinyl Alcohol-Polypropylene Hybrid Fibers. Journal of Industrial Textiles. 2016, Vol. 45, 5, pp. 637-651.

17. Liu, Huan and Zuo, Baoqi . Sound Absorption Property of PVA/PEO/GO Nanofiber Membrane and Non-woven Composite Material. Journal of Industrial Textiles. 2020, Vol. 50, 4, pp. 512-525.

18. Hong, Xinqiu, et al. Dry-wet spinning of PVA fiber with high strength and high Young's modulus.

Materials Science and Engineering. 2018, Vol. 439, 4, pp. 1-6.

19. Gao, Qiang, et al. Continuous wet-spinning of flexible and water-stable conductive PEDOT: PSS/PVA composite fibers for wearable sensors. Composites Communications. 2017, Vol. 17, pp. 134-140.

20. Li, Hongbin, et al. Hydrogen Bonding Governs the Elastic Properties of Poly(vinyl alcohol) in Water: Single-Molecule Force Spectroscopic Studies of PVA by AFM. Macromolecules. 2000, Vol. 33, 2, pp. 465-469.

21. Moulay, Saad. Review: Poly(vinyl alcohol) Functionalizations and Applications. Polymer-Plastics Technology and Engineering. 2015, Vol. 54, pp. 1289-1319.

22. Schoppner , V. and Kloke, P. Compounding, Encyclopedia of Polymer Science and Technology. New Jersey : John Wiley & Sons, Inc, 2002.

23. Wypych, George. Fillers in different processing methods. Handbook ofFillers. Toronto : ChemTec Publishing, 2016, pp. 968-1006.

24. Ku, Te-Hsing and Lin, Chin-An. Shear Flow Properties and Melt Spinning of Thermoplastic Polyvinyl Alcohol Melts. Textile Research Journal. 2005, Vol. 75, 9, pp. 681-688.

25. Vasanthan, N. Polyamide Fiber Formation: Structure, Properties and Characterization. Handbook of Textile Fibre Structure. USA : Woodhead Publishing, 2009, pp. 232-256.

26. Preparation and Properties of Chitosan–PVA Fibers Produced by Wet Spinning. Vega-Cázarez, Claudia A., et al. s.l.: Journal of Polymer Environment, 2018, Journal of Polymer Environment, Vol. 26, pp. 946-958.

27. Multifunctional composite fibers with conductive and magnetic properties. Li, Xin, et al. s.l. : Journal of Engineered Fibers and Fabrics, 2019, Journal of Engineered Fibers and Fabrics, Vol. 14, pp. 1-9.

28. Weise, Benjamin, et al. Melt- and Wet-Spinning of Graphene-Polymer Nano-Composite Fibres for Multifunctional Textile Applications. Materials Today Proceeding. 2017, Vol. 4, pp. 135-145.

29. Gao, Qiang, et al. Continuous wet-spinning of flexible and water-stable conductive PEDOT:PSS/PVA composite fibers for wearable sensors. Composites Communications. 2020, Vol. 17, pp. 134 -140.

30. Wang, Xinyue, Feng, Gu yu and Ge, Ming qiao. Influence of ethylene glycol vapor annealing on structure and property of wet-spun PVA/PEDOT:PSS blend fiber. J Mater Sci. 2017, Vol. 52, pp. 6917 -6927.

31. Xing, Cheng Yuan, et al. Poly (vinyl alcohol)/ β -Cyclodextrin Composite Fiber with Good Flame Retardant and Super-Smoke Suppression Properties. Polymers. 2020, Vol. 12, 5, pp. 1 - 14.

32. Menault, Jacques, Osugi, Tetsuro and Morimoto, Osamu. Polyvinyl Fibers. Ullmann's Polymers and Plastics: Products and Processes. Weinheim : Wiley, 2016.

33. Jee, Min Ho, et al. Effects of Wet-spinning Conditions on Structures, Mechanical and Electrical Properties of Multi-walled Carbon Nanotube Composite Fibers. Fibers and Polymers. 2012, Vol. 13, 4, pp. 443-449.

34. Piluso, Pierre, et al. Acetalization of Poly(vinyl alcohol) by a Fatty Aldehyde in Water Medium: Model Study, Kinetics, and Structure Analysis. Journal of Polymer Science, Part A: Polymer Chemistry. 2018, Vol. 56, pp. 661-671.

35. Nagarkar, Rigved and Patel, Jatin. Polyvinyl Alcohol: A Comprehensive Study. Acta Scientific Pharmaceutical Sciences. 2019, Vol. 3, 4, pp. 34-44.

36. Wu, Qian, Chen, Ning and Wang, Qi. Crystallization Behavior of Melt-spun Poly(vinyl alcohol) Fibers During Drawing Process. Journal of Polymer Research. 2010, Vol. 17, pp. 903-909.

37. Yamaura, Kazuo and Kumakura, Rie. Gelspinning of partially saponificated poly(vinyl alcohol). Journal of applied polymer science. 2000, Vol. 77, 13, pp. 2872-2876.

38. Fujiwara, Hiroshi, et al. Preparation of Highstrength Poly(vinyl alcohol) Fibers by Crosslinking Wet Spinning. Journal of Applied Polymer Science. 1989, Vol. 37, 5, pp. 1403-1414.

39. Dai, Lixing and Yu, Shaoyong. Effect of degree of saponification on structural and property change of poly(Vinyl alcohol) fibers. Polymers Advanced Technologies. 2003, Vol. 14, 7, pp. 449-457.

40. Kubo , Satoshi and Kadla, John F. The Formation of Strong Intermolecular Interactions in Immiscible

Blends of Poly(vinyl alcohol) (PVA) and Lignin. American Chemical Society. 2003, Vol. 4, 3, pp. 561–567.

41. Zhang, Hao, Wang, Qi and Li, Li. Dehydration of water-plasticized poly(vinyl alcohol) systems: particular behavior of isothermal mass transfer. Polymer international. 2008, Vol. 58, 1, pp. 97-104.

42. Chen, L N, Li, L and Wang, Q. New technology for thermal processing of poly(vinyl alcohol). Plastics, Rubber and Composites. 2007, Vol. 36, 7, pp. 283-290.

43. Xu, Yongjing, et al. The Preparation and Characterization of Plasticized PVA Fibres by a Novel Glycerol/Pseudo Ionic Liquids System With Melt Spinning Method. European Polymer Journal. 2020, Vol. 133, 15, pp. 1-10.

44. Peng, Fubing, et al. Novel nanocomposite pervaporation membranes composed of poly(vinyl alcohol) and chitosan-wrapped carbon nanotube. Journal of Membrane Science. 2007, Vol. 300, 1-2, pp. 13-19.

45. Lannoy, CF de, et al. A highly electrically conductive polymer–multiwalled carbon nanotube nanocomposite membrane. Journal of Membrane Science. 2012, Vols. 415 - 416, pp. 718-724.

46. Zhou, Weiping, et al. Elastic deformation of multiwalled carbon nanotubes in electrospun MWCNTs–PEO and MWCNTs–PVA nanofibers. Polymer. 2005, Vol. 46, 26, pp. 12689-12695.

47. Zhang, Xiefei, et al. Gel spinning of PVA/SWNT composite fiber. Polymer. 2004, Vol. 45, 26, pp. 8801-8807.

48. Yang, Zhiqian, et al. Fabrication and Characterization of Poly(vinyl alcohol)/Carbon Nanotube Melt-Spinning Composites Fiber. Progress in Natural Science: Materials International. 2015, Vol. 25, 5, pp. 437-444.

49. Mohamed, Shaimaa A., et al. Effect of ethylene carbonate as a plasticizer on CuI/PVA nanocomposite: Structure, optical and electrical properties. Journal of Advanced Research. 2014, Vol. 5, 1, pp. 79-86.

50. Xu, Yongjing, et al. The Investigation Plasticizing Mechanism on Poly (vinyl alcohol)/Water/Caprolactam System and the Preparation of Raw PVA Fibers by Melt Spinning. Earth and Environmental Science. 2020, Vol. 474, pp. 1-5.

51. Yan, Xiang, et al. Polypropylene/Poly(vinyl alcohol) Blends Compatibilized with Kaolinite Janus Hybrid Particles and Their Transformation into Fibers. American Chemical Society. 2019, Vol. 58, 25, pp. 10931–10940.

52. Qin, Qiange, et al. Structure evolution and performance of poly (vinyl alcohol) fibers with controllable cross-section fabricated using a combination of melt-spinning and stretching. Polymer Testing. 2022, Vol. 117, pp. 1-9.

53. Zhou, Ting, Wang, Meng and Chen, Ning. Study on Preparation of Triangular Melt-Spinning Poly (Vinyl Alcohol) Fibers and Its Fabric Strengthening and Toughening Epoxy. Polymers. 2021, Vol. 13, pp. 1-11.

54. Restrepo, Iván, et al. The Effect of Molecular Weight and Hydrolysis Degree of Poly(vinyl Alcohol)(PVA) on The Thermal and Mechanical Properties of Poly(lactic acid)/PVA Blends. Polímeros. 2018, Vol. 28, 2, pp. 169-177.

55. Uddin, Ahmed Jalal, Araki, Jun and Gotoh, Yasuo. Characterization of the poly(vinyl alcohol)/cellulose whisker gel spun fibers. Composites Part A: Applied Science and Manufacturing. 2011, Vol. 42, pp. 741 -747.

56. Jo, Yong Gu, et al. Effect of Gel Spinning Accompanied with Cross-Linking Using Boric Acid on the Structure and Properties of High-Molecular-Weight Poly(vinyl alcohol) Fiber. Journal of Applied Polymer Science. 2009, Vol. 113, pp. 1733–1738.

57. Li, Jingjing, et al. Fabrication of high strength PVA/rGO composite fibers by gel spinning. RSC Advances. 2014, Vol. 4, 82, pp. 43612 - 43618.

58. Lu, Chunhong, et al. Investigating the Structural and Mechanical Reinforcement Mechanism of Gel-Spun. North Carolina State University. 2017. Thesis.

59. Hong, Xinqiu, et al. Preparation and study of Polyvinyl Alcohol/Attapulgite nanocomposite fibers with high strength and high Young's modulus by gel spinning. Materials Research Express. 2020, Vol. 7, pp. 1 -8.

60. Peng, Jun, et al. Short cellulose nanofibrils as reinforcement in polyvinyl alcohol fiber. Polymer Engineering. 2014, Vol. 21, pp. 4287–4298.

61. Cha, Won-Ill , Hyu Hyon, Suong and Ikada, Yoshito. Gel Spinning of Poly(Vinyl Alcohol) from Dimethyl Sulfoxide/Water Mixture. Journal of polymer science-part B. 1994, Vol. 32, 2, pp. 297-304.

62. Sakurada, Ichiro and Dekker, Marcel. Polyvinyl alcohol fibers. Journal of Polymer Science Part C: Polymer Letters. 1985, Vol. 24, 9, pp. 485-486.

63. Jia, Erpeng, et al. Influences of Solution State on the Formation of Polyvinyl Alcohol As-spun Fiber during Dry-wet Gel Spinning. Fibers and Polymers. 2015, Vol. 16, pp. 1964 - 1969.

64. Hong, Xinqiu, et al. Preparation and characterization of high strength and high modulus PVA fiber via dry-wet spinning with cross-linkingof boric acid. Journal of applied polymer science. 2021, Vol. 138, pp. 1-8.

65. Zhu, Yin, et al. Study on the Chain Entanglement of Polyvinyl Alcohol Fiber during the Dry-Jet Wet Spinning Process. Fibers and Polymers. 2014, Vol. 16, pp. 345 - 353.

66. Chattopadhyay, R. Advances in textile yarn production. [book auth.] R. Alagirusamy and A. Das. Technical Textile Yarns - Industrial and Medical Applications. s.l. : Woodhead Publishing, 2010.

67. Miao, M. Fiber blending. Engineering of High-Performance Textiles. Australia : Elsevier, 2018, pp. 59-79.

68. Celep, Gizem and Yüksekkaya, Mehmet Emin. Comparison of thermal comfort properties of single jersey fabrics produced by hollow yarns with different hollowness ratio. The Journal of The Textile Institute. 2017, Vol. 108, 2, pp. 165-171.

69. Ünal, Pelin Gürkan and Üreyen, Mustafa E. Permeability properties of single jersey fabrics made of hollow yarns. Journal of the Textile Institute. 2017, Vol. 108, 11, pp. 1957-1965.

70. Aytaç, İlkem and Ünal, Pelin Gürkan. The effect of core-sheath proportion on the characteristics of hollow yarns: part I mechanical properties. The Journal of The Textile Institute. 2018, Vol. 109, 7, pp. 967-974.

71. —. The Effect of Core-Sheath Proportion on the Characteristics of Fabrics Produced with Hollow Yarns: Part II Comfort and Mechanical Properties. The Journal of The Textile Institute. 2018, Vol. 109, 7, pp. 975-982.

72. Ishtiaque, S. M., Das, A. and Singh, Reeti Pal. Packing of micro-porous yarns: Part I.Optimization of yarn characteristics. The Journal of The Textile Institute. 2008, Vol. 99, 2, pp. 147-155.

73. Badr, Alaa Arafa and El Nahrawy, Ashraf. Comfort Properties of Woven Fabrics Produced From Twist-Less Weft Using PVA Yarns. Mansoura Engineering Journal. 2015, Vol. 40, 2, pp. 1-14.

74. Lolaki, Asal, Shanbeh, Mohsen and Borhani, Sedigheh. Effect of structural parameters of porous

yarns and fabric on air permeability and moisture transfer of double-face woven fabrics. The Journal of The Textile Institute. 2017, Vol. 108, 6, pp. 992-1000.

75. Mukhopadhyay, Arunangshu, Ishtiaque, Saiyed Muzffar and Uttam, Devanand. Impact of Structural Variations on Pre-Hollow/Micro-Porous Yarn's Tensile and Physical Properties. Journal of Engineered Fibers and Fabrics. 2012, Vol. 7, 1, pp. 62-68.