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Use of citric acid-plasticized polyvinyl alcohol for cotton warp yarns cold sizing

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The properties of pure and citric acid-plasticized polyvinyl alcohol sizes in terms of viscosity, cohesive power, adhesive capacity, mechanical properties, and hairiness of sized yarns have been studied. Furthermore, pure and plasticized polyvinyl alcohol films are characterized by FTIR spectroscopy to describe intermolecular interactions. The morphology of sized yarns is studied by SEM images. It is confirmed that citric acid could enhance film properties, adhesion ability of polyvinyl alcohol to cotton fibres, hairiness, and mechanical properties of sized yarns. The desizeability of the prepared sizes is also checked and found high and efficient, which indicates that the citric acid-plasticized polyvinyl alcohol possess the application potential to cotton warp cold sizing.

Keywords: Citric acid, Cold warp sizing, Cotton yarns, Plasticizer, Polyvinyl alcohol, Warp yarn

1 Introduction

Textile sizing is a technological process of wet processing of warp yarns to obtain additional properties, which are necessary for weaving[1]. However, a large amount of steam energy is consumed for maintaining high temperature throughout sizing operation[2]. Thus, there is an urgent need to reduce the temperature of the sizing process for saving energy. Cold sizing is the technique used to prepare warp yarns for weaving by applying a cold size at room temperature without a drying process[3]. Cold sizing has been proved to be a good solution for reducing energy consumption in textile sizing[3, 4].

Polyvinyl alcohols (PVOH) have been considered as the biodegradable synthetic polymers widely used as textile sizing agents owning to their excellent film forming, emulsifying, and adhesive properties[5,6]. PVOH polymer, as a sizing agent, has high tensile strength and flexibility as compared with starch and modified starch sizes[7]. However, these properties are dependent on humidity. In other words, water that acts as a plasticizer for PVOH evaporate after the processing and the resulting films would be fragile for lack of plasticizers[8]. Therefore, in addition to water, the most common plasticizers used in PVOH based formulation are polyols, such as glycerol[9-11], urea, and salts[12,13]. These plasticizers could increase the mobility and the free volume of the PVOH molecular chains; thereby the flexibility of the resulting films was improved. One of the most important properties of an efficient plasticizer is to be compatible with the polymer matrix. Thus, several other plasticizers, such as polyethylene glycol, sorbitol, and citric acid, have also been successfully employed[14].

Citric acid (CA) with one hydroxyl and three carboxyl groups exists widely in citrus fruits and pineapples, where it is rated as an inexpensive and non-toxic organic acid. CA has been used as a plasticizing agent to improve the performance of starch and (PVOH/starch) blends. For instance, the presence of two types of functional groups in CA could increase the inter/intramolecular interactions between starch, PVOH, and CA better than glycerol and sorbitol[15]. Shi *et al.*[16] examined the citric acid as a plasticizer for thermoplastic starch. They founded that CA may improve the mechanical properties and water resistibility. Besides, Zou *et al.*[17] performed similar studies using citric acid as a plasticizer for starch and PVOH composites. Generally, citric acid has been used as a plasticizer and crosslinking agent of starch/PVOH based composite films for wound dressing application[18], bioactive food packaging industry[19], and biomedical fields[20]. Despite these non-toxic properties and good compatibility with polysaccharide polymers, the CA plasticizing agent remains unexplored for textile applications, especially as an additive in warp sizing recipes. Therefore, there

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are no specific studies about using CA as a plasticizer of polyvinyl alcohol used as an adhesive for the textile warp sizing process. On other hand, there are a few papers about cold warp sizing of pure cotton yarns[3, 21]. Thus, no investigations have been reported using citric acid (CA) as a plasticizer agent in PVOH sizing recipe of cotton warp yarns cold sizing to enhance the sizing efficiency.

Accordingly, the purpose of the present work was to evaluate the influence of citric acid as an eco-friendly plasticizer of polyvinyl alcohol and to investigate the combined effects of them on cotton warp cold sizing process efficiency. The citric acid (CA) was chosen as the additive for the reason of its multi-carboxylic structure, which could make a good interaction between carboxyl groups of CA and hydroxyl groups of PVOH. Consequently, such an interaction would improve the functional properties of PVOH used as sizing agent of warp yarns. The impact of CA content on viscosity and cohesion power of the PVOH size, the adhesion capacity of the cold size to cotton fibres, the add-on, tensile strength, and elongation of cold-sized cotton yarns are comparatively studied in this work. The above-mentioned warp sizing properties are key factors in assessing weaving performance[1]. The intermolecular interactions between PVOH/CA are analyzed by Fourier Transform Infrared (FTIR), and by Scanning Electron Microscopy (SEM). Finally, the optimum citric acid (CA) content (which is 5%) in cold sizing solution is specified.

2 Materials and Methods

2.1 Materials

Raw cotton roving with a linear density of 1.1 ktex used as a substrate for adhesion measurement, was offered by SITEX industry (Sousse, Tunisia). The average length and fineness of cotton fibres in the roving were 29.1 mm and 1.59 dtex respectively. The cold sizing process was performed on 100% raw cotton carded yarns with yarn count of 11.5 Nm and twist of 473 turns/m.

Polyvinyl alcohol (PVA2488) with a degree of hydrolysis of 87-89% and molecular weight average of 24,000 g/mol and citric acid were purchased from Sigma Aldrich. Distilled water was used in all experiments.

Laboratory-padding apparatus, which simulates the sizing machine, was used for the cold sizing procedure. The padding machine was equipped with a size box, a dipping roller, and a pair of squeezing rollers enabling regulation of the squeezing pressure.

2.2 Preparation of Cold Sizing Solution

When the temperature of the reaction vessel containing distilled water was increased to 65°C, 50 g/ L of PVOH granules were added slowly with continuous stirring. The addition of PVOH granules was stopped when the temperature of the reaction vessel approached 85°C. Simultaneously the supply of heat was stopped; however stirring was continued. When PVOH formed a homogeneous solution, a different CA content (0, 5, and 10% W/W based on the weight of PVOH) was added to the above preparation with continuous stirring for 30 min.

2.3 Viscosity Test

A rheometer (Rheotec RC 30-CPS) was used to determine the viscosity of the PVOH sizing solution at various conditions. A C-25 cone spindle was used for each measurement (shear speed=1000 s^{-1}). Viscosity measurements (mPa.s) were done at 25°C according to ISO 6388. Three separate measurements were done for each sample and the average and ± one standard deviation are reported.

Viscosity stability (S_η, %) of prepared PVOH size was expressed as a percentage of invariance in apparent viscosity of the size solution over a period of 2 h at the temperature indicated. The stability was measured over the period following the paste maintenance, during which the viscosity readings were taken after every 30 min. The stability was calculated using the following equation :

$$S_\eta\ (\%) = [1- (\eta_{max} - \eta_{min})/\ \eta]*100 \qquad \dots (1)$$

where η is the viscosity of prepared PVOH size; and η_{max} and η_{min} , the maximum and minimum of the viscosities measured over the period respectively.

2.4 Film Preparation and Tensile Properties Testing

The cohesion power of a sizing material, as examined by Behera *et al.*[7], was tested by analyzing the tensile properties of size film. Approximately 10 mL of the prepared size solution was cast into Petri dishes and dried in normal atmospheric conditions. Tensile strength (TS) and Elongation-at-break (E%) of size films were determined according to ASTM standard D882 on a Lloyd LR5K tensile tester. Twenty film strips of (10 mm × 80 mm) size for each condition were tested and the average values were presented. TS was calculated by dividing the maximum load P (N) by the cross-sectional area (m²) as follows:

$$TS\ (MPa) = P/\ (b*d) \quad \dots (2)$$

where P is the maximum load (N); b, the sample width (mm); and d, the film thickness (mm). The thickness of films was determined as an average of five positions of the film samples using a digital micrometer with an accuracy of 0.01 mm.

2.5 Adhesion Capacity

The ability of the sizing solution to adhere the fibres together was used as an assessment of the inter-fibre adhesion or adhesion capacity. As roving is a bundle of loose fibres without strength, the improvement in the strength of the roving after sizing is considered to be an indication of the adhesion of the size to the fibre substrate[18]. To test the compatibility of the size recipe with cotton fibre substrate, the 100% cotton roving was sized with different size formulations, and subsequently tested by a tensile tester (model Lloyd LR5K) with a gauge length of 100 mm and a crosshead speed of 50 mm/min. Then, the adhesion capacity was evaluated in terms of maximum strength (Sm), breaking extension (Eb), and work-to-break (Wb) of a slightly sized roving. About 20 samples for each condition were measured and their mean values were calculated

2.6 Cold Sizing Process, Add-on (%) Determination, and Tensile Properties

The process of cold sizing of cotton yarns was carried out on a laboratory-padding machine. The size concentration in the box was 50 g/ L, the sizing speed was maintained at 2-3 m/min, and the squeezing pressure was 20 N/cm², drying of the sized warp yarns was carried in air ambient. Cold-sized and unsized yarns were conditioned for at least 24h before property testing. Add-on (%) was calculated by taking the weights of the oven-dried sized and unsized yarn samples of around 10 m of length, with 3 readings per sample by using the following equation:

Add-on %= [(weight of sized yarn-weight of unsized yarn)/ weight of unsized yarn]×100 … (3)

Yarns tensile properties were tested on Lloyd tensile tester according to ISO 2062. For each sample, twenty pairs of tensile strength TS (N) and breaking elongation BE (%) readings were measured and their mean values were calculated. The hairiness index value of unsized and cold-sized samples with different size formulations was tested on shirley electronic yarn hairiness tester according to ASTM D5647 standard test method. Each sample's appearance was observed using the LEICA M50 optical transmission microscope.

2.7 SEM and FTIR Analyses

The morphology of yarns cross-section was observed under Thermo Scientific Q250 scanning electronic microscope (SEM) at an acceleration voltage of 15.0 kV. The infrared spectra of pure PVOH film and CA-plasticized PVOH films were detected on an FTIR spectrophotometer (model Perkin Elmer UATR Two). The scans were carried at a resolution of 4.0 cm^{-1} and in wave number 4000-400 cm^{-1}.

2.8 Desizing Studies

Fabrics sized with different recipes with a known amount of add-on were desized using a non-ionic detergent at a concentration of 2g/L and ratio of 1:30. After its aqua solution was heated up to 40°C-50°C, sized samples were added and treated for 30 min. Finally, the samples were rinsed and then dried in the air. Weights of samples before and after desizing were taken to determine the desizing degree (%) based on the following equation:

Desizing degree % = [(weight of fabric after rinse-weight of desized fabric)/ (weight of fabric before desizing× add-on %)]×100 … (4)

To evaluate the efficiency of desizing process, the wettability of cotton fabric after and before desizing was tested using a DSA25 drop shape analyzer (KRÜSS GmbH – Germany). The wettability was determined through Water Angle Contact (WAC) and Water Absorption Time (WAT) by the sessile drop method.

3 Results and Discussion

3.1 Effect of CA Content on Size Solution Viscosity

The apparent viscosity of PVOH solutions with different CA contents in the sizing formulation, their coefficients of variance CV (%), and their stability $S\eta$ (%) are shown in Table 1. It is found that the pure

Table 1 — Influence of CA content on PVOH viscosity

Property	0 %	5 %	10 %
Viscosity (η), cP	114,4	87,84	90,5
CV, %	0,802	0,353	0,704
S_η, %	94,03	90,42	93,39

0%, 5%, and 10% are CA contents.

PVOH solution has the greater viscosity (114 cP), which is due to the promotion of a large number and stronger inter-molecular association. According to Li *et al.*[22], the apparent viscosity is directly influenced by molecular structure, molecular weight, and internal friction among molecular chains of the polymer. It is also noteworthy that viscosity decreases significantly by adding 5% of CA to the PVOH size solution (from 114 cP to 87 cP) and slightly increases from 87 cP to 90 cP by increasing CA content from 5% to 10%. This decrease in viscosity might be the result of the destruction of some intermolecular PVOH chains by incorporating the plasticizer agent, which will enhance the free volume and weaken the original interactions of PVOH. Wenqian *et al.*[23] also reported that the incorporation of polyol plasticizers into PVOH matrix decreases the viscosity.

A moderate viscosity of size solution is advantageous because sizes with lower viscosity could not well penetrate onto yarns, while high viscosity sizes will hardly penetrate into the yarn. Therefore, the moderate viscous paste will penetrate easily into the yarn and give a good cover with penetration that will not be removed easily during the abrasion of warp yarns on the loom. The results of S_η (%) of pure PVOH and CA plasticized PVOH solutions are presented in Table 1 and it shows high values compared with acid-thinned starch[24]. Thus, a high S_η (%) of the size solution gives stable add-on (%) warp yarn sizing.

3.2 Effect of CA Content on Cohesion Property of PVOH

Cohesion property has been measured by testing the tensile properties of the size films. The mechanical properties of pure and plasticized PVOH films with different CA contents are shown in Fig. 1. It is found that with an increase in plasticizer content, the tensile strength of PVOH film is decreased, while the elongation of PVOH film is enhanced significantly. Pure PVOH is crystalline and consists of layers of chains joined together by molecular bonds with the presence of amorphous regions, formed between the layers. However, when CA as plasticizer is added, the interactions between CA and the PVOH matrix lead to an increasing degree of amorphous regions among PVOH macromolecules, which leads to the decreased crystallinity, and as a result, reducing the tensile strength of CA plasticized PVOH films. Maatoug *et al.*[25] have reported that the concentration of glycerol as a plasticizer agent affects the mechanical properties of sizing films, which shows the lowest values for tensile strength.

On the other hand, the CA-plasticized PVOH films show flexible character compared to the pure PVOH films. According to the theory of free volume, the incorporation of plasticizers would increase the free volume of PVOH. Hence, the movement of PVOH molecules would be easy and the flexibility of PVOH would be improved. Shi *et al.*[26] have reported similar changes in the performance of CA as a plasticizer agent. They cast a series of starch–PVOH films with varying concentrations (5–30 wt%) of citric acid. They found that when citric acid is added, the tensile strength is decreased from 48 MPa to 42 MPa, and the elongation at break is increased from 102% to 208%. As demonstrated by Behera *et al.*[7], size film elongation is more important than film strength, because flexibility is more significant than strength from a weaving point of view, which justifies the necessity of using plasticizer agent in size recipe to improve sizing efficiency.

3.3 Effect of CA Content on Adhesion Capacity of Size Material to Cotton Fibres

The weavability of sized yarns is greatly influenced by the adhesion power of the size material, which enhances the strength of sized yarns by bonding the fibres together, and it can reduce yarn hairiness. Thus, adhesion is an important parameter to select the suitable size material[21]. Therefore, to study the effect of plasticizer content on adhesion power of PVOH,

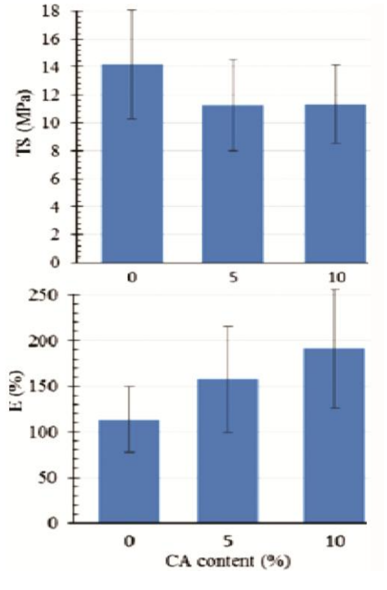

Fig. 1 — Effect of CA content (%) on (a) tensile strength (TS), and (b) elongation (E) of PVOH films

the mechanical test of sized roving is carried and the results are presented in Table 2. It is observed that adding 5% of CA improves significantly adhesion property of PVOH, and increasing CA content to 10% reduces slightly the adhesion.

Simultaneously, pure PVOH size and 5% CA-plasticized PVOH size present 83 N and 92,3 N as maximal strength, 9 % and 9.5 % as breaking elongation, and 0.41 J and 0.45 J as work-to-break values. The enhancement of adhesion characteristics with adding 5% CA is undoubtedly due to the plasticization phenomena. Moreover, the presence of plasticizer in polymer solution improves the motion of PVOH molecules. Thus, the enhanced movability promotes the diffusion and access of PVOH molecules into fibre substrate, which increases the adhesion property of the size. On the other hand, the small decline of adhesion property with increasing CA content from 5% to 10% may be due to the slight increase of size viscosity (Table 1), which reduce the accessibility of size into fibre and consequently diminish the adhesion capacity of the CA-plasticizer PVOH. Furthermore, the difference in adhesion between 5% CA-plasticized and 10% CA-plasticized PVOH is acceptable (not significant) as compared to the un-plasticized PVOH. Thus, 5% CA shows the potential to enhance PVOH cold sizing adhesion.

3.4 Effect of CA Content on Add-on and Tensile Strength of Unsized and Sized Yarns

The add-on, which is a critical parameter that determines the sizing result, has been studied as a function of CA content as a plasticizer. Figure 2 gives size add-on values of yarn and indicates that the rising of citric acid content in the PVOH solution increases the add-on. The improvement of add-on with an increase of CA content is probably due to the formation of hydrogen bonds between PVOH and CA molecules, which will decrease the density of the intermolecular hydrogen bonds in PVOH polymer, and consequently will lead to reduced intermolecular forces[27]. Accordingly, the number of hydroxyl groups is increased with increasing CA content, which enhances the wettability of cotton fibres in the CA-plasticized PVOH and increases the add-on value.

Table 2 — Influence of CA content on maximal strength (Sm), breaking extension (Eb), and work to break (Wb) of PVOH cold sized roving

Property	0%	5%	10%
Sm, N	83.00 (±0,02)	92.30 (±0,06)	90.00 (±0,02)
Eb, %	9.00 (±0,06)	9.50 (±0,05)	8.90 (±0, 08)
Wb, J	0.41 (±0,05)	0.45 (±0,05)	0.40 (±0,05)

0%, 5%, 10% are CA contents.

Tensile strength TS (N) and breaking elongation BE (%) of unsized and sized cotton yarns with PVOH in presence of different CA content are shown in Table 3. It is observed that after cold sizing with pure PVOH solution, the tensile strength is increased from 11.10 N to 17.26 N, and the breaking elongation decreases from 10.48 % to 8.04 %. This is due to the diffusion of the size material into the yarn body, which makes the yarn more rigid. Also, it is deduced from Table 3 that the tensile strength and breaking elongation of sized yarn are improved by adding 5% of CA to the size solution, but it is slightly reduced with the increase of CA content to 10%.

Probably, the tensile properties enhancement is a result of improved fibre/size adhesion, due to increase of hydroxyl groups by adding plasticizer, and thus raised cohesion among fibres in the yarn. Wang *et al.*[28] found similar results and have shown that the CA, as a plasticizer, could increase the macromolecular mobility of the polymer, and as a result, the polymeric networks become less dense due

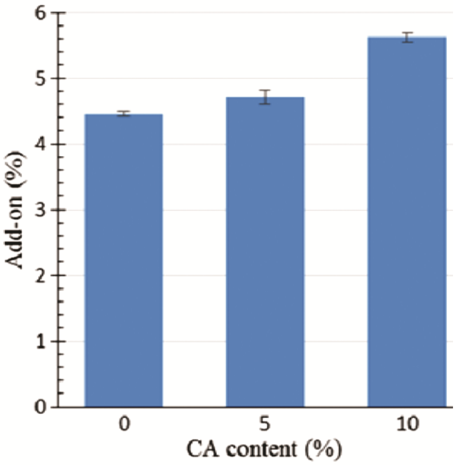

Fig. 2 — Effect of CA content (%) on add-on of PVOH cold sizes

Table 3 — Tensile properties of unsized and cold sized cotton yarns by PVOH with different CA content

Samples	Unsized	CA0	CA5	CA10
TS, N	11.10	17.26	18.26	17.64
CVs, %	5.58	5.55	4.62	4.70
BE, %	10.48	8.04	9.55	8.98
CVe, %	5.00	5.93	6.65	5.37

CA0, CA5, and CA10 are respectively yarn samples cold-sized with pure PVOH, 5% CA-plasticized PVOH, and 10% CA-plasticized PVOH.

CVs (%) and CVe (%) are coefficients of variance of tensile strength and breaking elongation.

to the decrease in intermolecular forces. Thus, the diffusion of the size into the yarn body is enhanced and the tensile properties of sized yarns are improved. However, the small reduction of tensile properties of yarns sized with 10% CA-plasticized PVOH has resulted in a slight increase of viscosity (Table 1).

3.5 Hairiness and Surface Observation of Cotton Yarns Before and After Cold Sizing

Both hairiness index value and the appearance observation have been done to evaluate the reduction of cotton hairs after sizing. The hairiness index values tested on Shirley electronic hairiness tester for unsized and cold-sized cotton yarns with different PVOH formulations are shown in Fig. 3. The hairiness index value is the number of hairs larger than 3mm in length present in one meter of yarn. It is observed from Fig. 3 that the hairiness of cotton yarn decreases after cold sizing from 100 hairs/m to 47 hairs/m. This is due to the covering of the yarn surface by the size film, which bound the protruded fibres in the surface to the yarn body. Besides, it can be seen that the cotton hairs are decreased from 47 hairs/m to 30 hairs/m by adding 5% (w/w) of CA to the PVOH cold sizing recipe. The hairiness value reduction is the result of enhancing penetration of the 5% CA-plasticized PVOH with the decrease of its viscosity. Reduced size viscosity is advantageous because the less viscous size will penetrate easily into the yarn with a good cover of the yarn surface, which will make protruding hairs bound into the yarn. Li *et al.*[29] also reported the same conclusion. They found that the hairiness amount of the sized yarns is closely dependent on the size viscosity, and a sizing agent with low viscosity can easily permeate through the yarn and increase inter-fibre cohesive force.

Figure 4 shows the photographs of raw yarn and sized yarns with pure and CA-plasticized PVOH. The

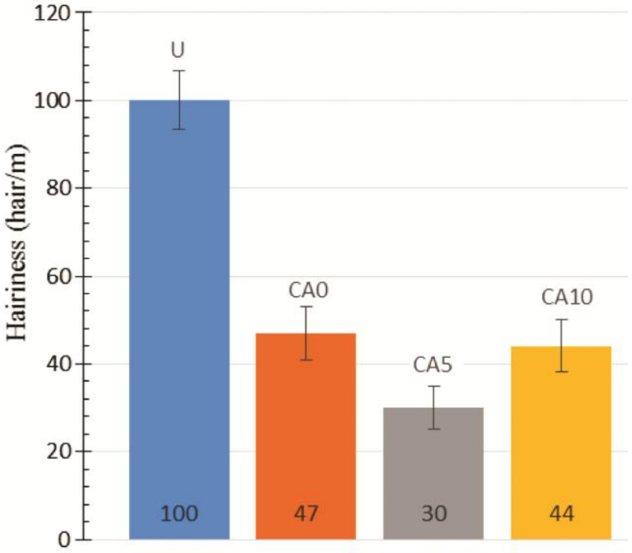

Fig. 3 — Hairiness index values of unsized yarn (U), pure PVOH (CA0), 5% CA-plasticized PVOH (CA5), and 10% CA-plasticized PVOH (CA10) cold sized cotton yarns

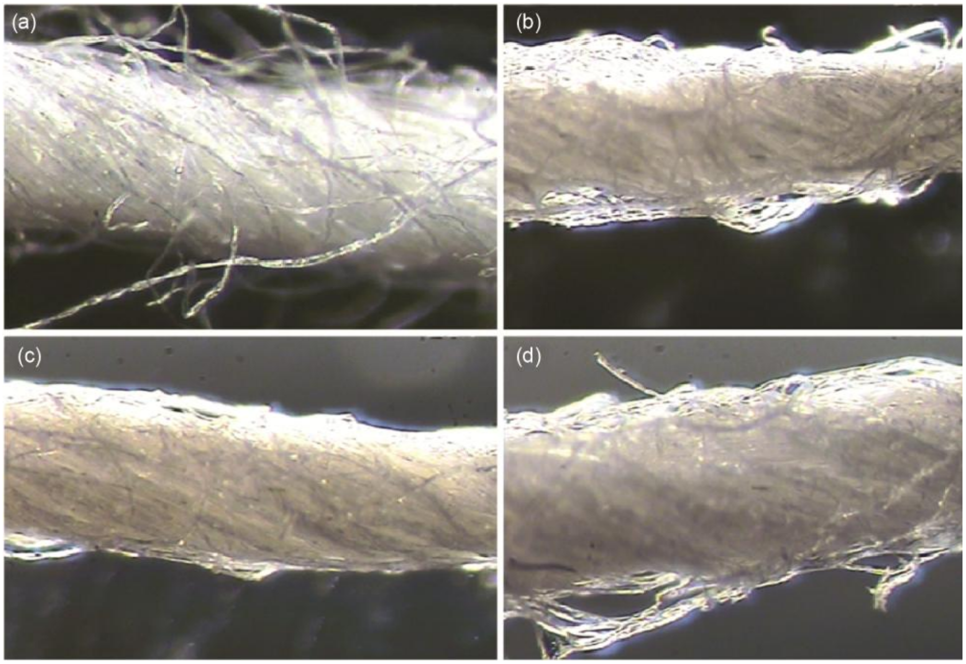

Fig. 4 — Photographs (magnification × 40) of unsized yarn (a), yarn sized with pure PVOH (b), yarn sized with 5% CA-plasticized PVOH (c), and yarn sized with 10% CA-plasticized PVOH (d)

hairiness index values obtained in this study are also supported by the yarns observations (Fig. 4). Thus, the improved size penetration by adding 5% CA is responsible to facilitate adhesion of the protruded fibre ends on the surface to the bulk of the yarn, as shown in Fig. 4(c), which reduces the hairiness index value of the cold sized yarn.

3.6 Morphological Observations of Unsized and Cold Sized Yarn

Figures 5(a)-(c) are the cross-section morphology of raw cotton yarn, cotton yarn sized with pure PVA, and cotton yarn sized with 5% CA-plasticized PVA, respectively. Fig 5(d) reflects the micrographs of raw cotton fibres. Figs 5 (e) and (f) show fibre/size interactions of pure PVA and 5% CA-plasticized PVA sized fibres. The morphology of the unsized fibres, which show a loose character, can be easily identified. Fibres at the edge of cold-sized yarn are stuck together by the pure PVOH, as shown in Figs 5(b) and (e), but the fibres in the center of the yarn are not heavily coated with the size [Fig. 5 (b)]. When 5% CA is added to PVOH, a compact structure with fibres more glued together is noticed [Figs 5 (c) and (f)]. Also, as demonstrated in Fig. 5 (c), it is found that the 5% CA-plasticized PVOH is well dispersed in the cotton yarn structure matrix without large accumulation. The improved dispersion and compatibility between plasticized PVOH size and cotton fibres can be due to similarity in the chemical structure of the cellulosic fibre, PVOH as a size, and CA as a plasticizer. Therefore, the homogeneous dispersion of plasticized PVOH in the cotton fibres plays an important role in improving the mechanical properties of sized yarns, which is expected also to play an important role to enhance the warp yarn sizing efficiency.

3.7 Analysis of Composition in CA-Plasticized PVOH Films and Sized Cotton

The interactions between PVOH and CA are analyzed by FTIR spectra. The FTIR results of pure PVOH film and CA-plasticized PVOH films are shown in Fig. 6. The spectrum of the pure PVOH film exhibits a broad band at 3273cm^{-1}, which corresponds to the O-H stretching vibration[30]. Two bands at 2921 cm^{-1} and 2854 cm^{-1} are attributed to the asymmetrical and symmetrical stretching of C-H groups[31] respectively. The small peak at 1732 cm^{-1} is assigned to the carbonyl group, a peak at 1427 cm^{-1} is resulted from the in-plane deformation of -CH2- bonds, and a peak at 1243 cm^{-1} attributed to C-H wagging vibrations were observed[32]. The peaks at approximately 1088 and 1024 cm^{-1} are due to the C-O stretching vibrations and C-C-C stretching vibration[33], respectively. The absorption bands at 946 cm^{-1} and 842 cm^{-1} approve the symmetric stretching of the C-O-C group[34]. Compared with the spectra CA0, the

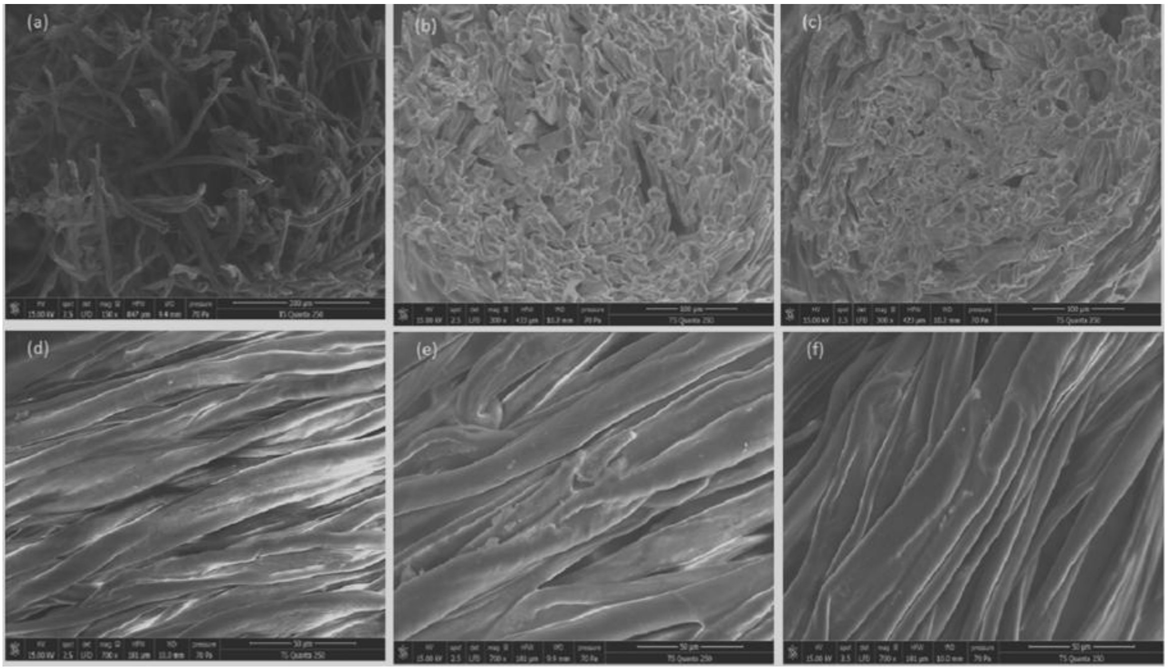

Fig. 5 — Cross-section and fibres images of raw yarn (a)/ (d), yarn sized with pure PVOH (b)/ (e), and yarn sized with 5% CA plasticized PVOH (c)/ (f)

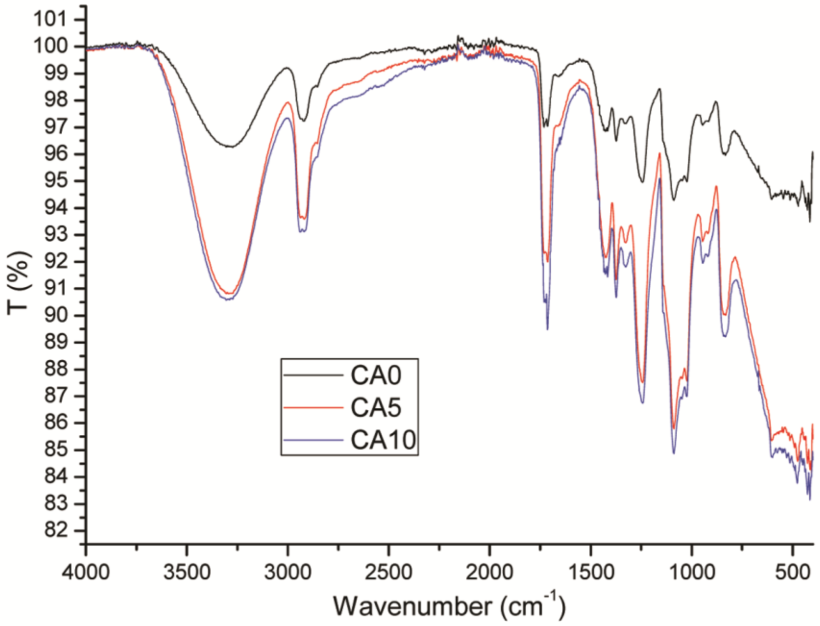

Fig. 6 — FTIR spectra of pure PVOH film (CA0), 5% citric acid plasticized PVOH film (CA5), and 10% citric acid plasticized PVOH film (CA10)

FTIR spectra of the plasticized film (CA5 and CA10) show peak at 1713 cm^{-1}, which is attributed to the carbonyl group C = O. This peak indicates the ester bonds between COOH groups of citric acid and OH groups on PVOH[35]. Sabzi *et al.*[36] also reported a similar result, where the formation of crosslinks by citric acid on PVOH showed the absorption bands at 1722 cm^{-1}. This peak is probably originated from both the esterification reaction between PVOH and CA, and free carboxylic acid groups remained on CA[26,28]. Moreover, the hydroxyl absorption band becomes stronger in the presence of CA5 and CA10 (Fig. 6). The intensity decrease of the peak at 3273 cm^{-1} from 96.00% to 90.82 % and to 90.58 %, by adding 5% and 10 % CA respectively, indicates the enhanced hydrogen-bond inter-actions due to the formation of ester bonds by citric acid[37]. Thus, in the spectrum of CA5, the intensity of the peak related to the stretching vibration of OH groups of PVOH is reduced as compared to pure PVOH due to their condensation with the COOH functional groups of CA. On the other hand, with raising the CA content from 5% to 10%, the intensity of this peak is kept constant, which indicates that the intermolecular interaction between PVOH and CA hydrogen bond does not show any enhancement by moving from 5% to 10% CA. These results are consistent with the mechanical properties of pure and CA-plasticized PVOH films (Fig. 1).

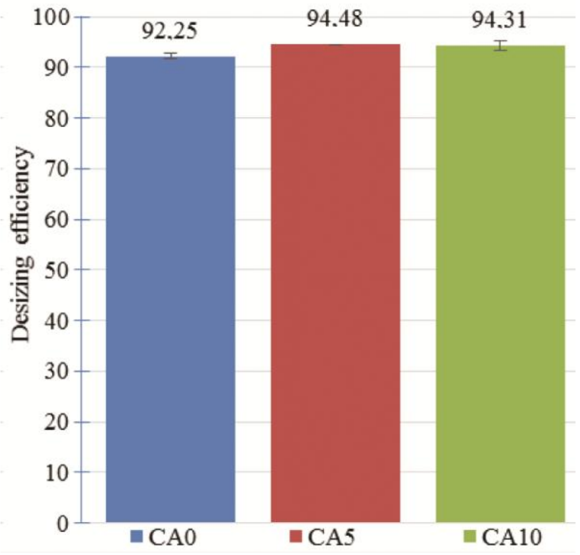

Fig. 7 — Desizing efficiency of un-plasticized PVOH (CA0), 5% CA-plasticized PVOH (CA5), and 10% CA-plasticized PVOH (CA10).

3.8 Desizing Efficiency and Wettability Studies

The size onto warp yarns must be removed after weaving and before dyeing, printing, and finishing. Insufficient removal of the size induces fabric with a hard handle and causes stains compromising fabric appearance and subsequent processing. As a result, easy desizeability is one of the essential requirements for any kind of warp sizes[38]. Therefore, a desizing property of the size is accessed. Fig. 7 illustrates that

Table 4 — Wettability analysis of cold sized and desized cotton fabrics by PVOH with different CA content

Property	0%	5%	10%
Sized samples			
WAC, deg	94 (±15)	85 (±12)	93 (±10)
WAT, ms	1120 (±200)	1764 (±181)	1555 (±352)
Desized samples			
WAC, deg	63 (±5)	62 (±4)	68 (±5)
WAT, ms	317 (±44)	336 (±65)	314 (±59)

0%, 5%, 10% are CA contents.

the fabrics sized with PVOH show satisfactory desizeability with greater than 90% size removal even with CA-plasticized PVOH. No major difference is observed between pure and CA-plasticized PVOH, which means that the presence of CA in the size recipe would not affect the removing process after weaving. On other hand, easy removal of the size is important to facilitate further processing of the fabrics. Besides, the wettability properties of cotton fabric before and after desizing are analyzed to judge the desizing efficiency.

According to the results shown in Table 4, the water angle contact (WAC) of pure PVOH, 5% CA-PVOH, and 10 % CA-PVOH sized samples are 94°, 85°, and 93° respectively. After desizing, the WAC decreases markedly to 63°, 62°, and 68° respectively. For desized samples, the water droplets are absorbed intensely into the fabric as compared to samples before desizing. This phenomenon indicates that cotton fibres are endowed with superior wettability by desizing treatment. Therefore, the hydrophilicity of the fabrics is significantly improved. This is due to the efficient removal and cleaning of the applied sizing agent.

4 Conclusion

From this study, it has been concluded that citric acid (CA), which is a green and organic product, presents an excellent plasticizer effect in polyvinyl alcohol (PVOH) as a cold sizing agent for cotton fibres. The mechanical properties of PVOH films, obtained using a casting method with CA as a plasticizer, are tested to determine the cohesive power of the size. The increase of citric acid content in PVOH solution decreases the viscosity from 114 cP to 90 cP, decreases the tensile strength of film from 14.19% to 11.34 MPa, and increases the film elongation (from 113 to 191%). Furthermore, the addition of CA as a plasticizer to the PVOH has enhanced the adhesion power of the size, the size add-on, the tensile strength, and elongation at break of sized yarns, while there is a reduction in sized yarn hairiness. These results are also confirmed from scanning electronic microscopic images of cotton yarn before and after sizing with PVOH sizing. Besides, FTIR analyses of the pure PVOH film, PVOH/CA films, raw cotton fibres, and cold-sized cotton fibres are also carried and proved the strong interactions of the OH groups of the PVOH, CA, and cotton fibres. Improvements in cold sizing efficiency are observed due to the good interaction of the CA-plasticized PVOH with cotton fibres due to a similar chemical structure. Hence, this study approves the recommendation that citric acid (CA) is a good plasticizer for the polyvinyl alcohol (PVOH) to cotton warp yarns for cold sizing.

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