ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 32, No. 1. 2026

Grafting Poly(hydroxyethyl acrylate) Branches onto Polyvinyl Alcohol to Promote its Adhesion and Film Properties

Wei LI [*]**, Yue ZHANG, Xun ZHANG, Yifan ZHANG, Xiaolong CHENG, Xuchen TAO**

College of Textiles and Garments, Anhui Polytechnic University, Wuhu 241000, Anhui Province, PR China

http://doi.org/10.5755/j02.ms.39632

Received 29 November 2024; accepted 8 April 2025

The objective of this study was to survey the influence of the grafted poly(hydroxyethyl acrylate) (PHEA) branches on the sizing properties (adhesion and film properties) of PVA1799 to determine if the branches can improve the sizing properties and develop a new PVA-based size (PVA1799-*g*-PHEA) with a suitable grafting ratio for potential use in polyester/cotton warp sizing. The sizing properties of PVA1799-*g*-PHEA were estimated compared with PVA1799. The PVA1799-*g*-PHEA samples with the grafting ratios of 3.53 %, 6.74 %, 7.04 %, and 7.34 % were synthesized through graft polymerization of PVA1799 with different masses of HEA monomers at 40 °C using the Fe^{2+}-H_2O_2 redox system by a dry process. The sample was characterized by Fourier transform infrared (FTIR), scanning electron microscopy (SEM), and thermogravimetric (TG) analyses. FTIR analysis confirmed the successful incorporation of PHEA branches, SEM analysis pointed out that the surface morphology of PVA1799-*g*-PHEA and PVA1799 had no obvious difference, and TG analysis revealed that incorporating the PHEA branches promoted the thermal stability of PVA1799. Compared to PVA1799, the PVA1799-*g*-PHEA exhibited significantly higher bonding forces with polyester/cotton roving and greater film elongation. It also displayed a slight increase in film strength and a reduced film break time when exposed to hot water. This suggests that incorporating PHEA branches can enhance the sizing properties and desizability of PVA1799. These improvements were further enhanced by increasing the grafting ratio. Notably, the PVA1799-g-PHEA with the 7.34 % grafting ratio showed promising potential for sizing polyester/cotton warp yarns.

Keywords: PVA, graft polymerization, adhesion, film properties.

1. INTRODUCTION

During the weaving process, warp yarn experiences friction with adjacent yarns and mechanical components and repeated stretching and bending [1]. These issues can pull fibers from the yarns, damaging their structure and increasing breakage rates, which negatively impacts loom efficiency [2]. Therefore, most short- and long-filament warp yarns must be sized with textile sizes before weaving.

Currently, starch-based polymeric materials as textile sizes have been widely adopted in textile sizing [3] due to their natural renewability [4], good biodegradability [5], and low price [6]. Another main textile size is polyvinyl alcohol (PVA); its main chain is a carbon chain containing numerous hydroxyl groups, which makes the PVA show strong polarity and have many hydrogen bonds [7]. PVA has good water solubility [8,9] and permeability [10] and can form a tough film with strong wear resistance, making it attractive in fields such as textile sizing [11]. However, PVA also has some disadvantages. For example, the PVA1799 has the main disadvantages such as easy skinning of the paste, difficulty of desizing, and being mainly suitable for sizing hydrophilic fiber yarns. These issues limit its application in the sizing application.

The graft polymerization between polymers and vinyl monomers has become an important technique for attaching synthetic branches to polymer molecules [12]. This technique has been considered one of the most important techniques for strengthening the properties of starch used in warp sizing [13]. The prepared grafted starches have been used to some extent in warp sizing [14] and paper making [15]. Nevertheless, no clear research is available about the utilization of grafted PVA1799 in the warp sizing application in recent years. Hydroxyethyl acrylate (HEA) containing hydroxyl and ester groups can be used as a monomer for attaching the poly(hydroxyethyl acrylate) (PHEA) branches onto PVA1799 chains. The branches may obstruct the hydrogen bonding between PVA1799 hydroxyls and increase the distance between PVA1799 chains, which favors penetrating the water into the matrix of PVA1799 film or layer formed between the fibers within roving or yarns. Accordingly, the PHEA branches may be expected to improve the desizing of PVA1799. In addition, the hydrophilic hydroxyl and hydrophobic ester groups in the HEA units make the PHEA branches exhibit an amphiphilic characteristic, inducing a lowered surface tension for the PVA1799 paste and favoring enhancing its wetting and spreading at the fiber surface, which is beneficial to the simultaneous bonding of PVA1799 to both hydrophilic and hydrophobic fibers. As a result, the HEA monomer is selected to modify PVA1799 to improve its properties. The molecular structure of the prepared PVA1799-*g*-PHEA is presented in Fig. 1. So far, no studies have conveyed the influence of the PHEA branches on the sizing properties (adhesion and film properties) of PVA1799. As a result, this study aims to determine if the branches can improve the sizing properties and attain a suitable grafting ratio of PVA1799-*g*-PHEA for its potential use in polyester/cotton warp sizing.

---

[*] Corresponding author: W. Li
E-mail: *liw@ahpu.edu.cn*

2. EXPERIMENTAL DETAILS

2.1. Materials and reagents

PVA1799, containing a volatile matter content of 5.37 %, was supplied by Shuangxin Environmental Protection Materials Co., Ltd. (Nei Monggol, China). Polyester/cotton (65/35 in blending ratio, 775 tex) roving applied to assess the adhesion was offered by Anhui Huamao Textile Co., Ltd. (Anhui, China).

Analytical reagents: HEA, anhydrous ethanol, hydrogen peroxide, ammonium ferrous sulfate, etc., were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

2.2. Synthesis of PVA1799-*g*-PHEA

Under a dry process, the graft polymerization of PVA1799 with HEA monomer was conducted to synthesize the PVA1799-*g*-PHEA, as illustrated in Fig. 1. The 120 g of PVA1799 was first crushed by the pulverizer and then ground with a mortar. The prepared ammonium ferrous sulfate solution (28 g, 0.5 wt.%), hydrogen peroxide aqueous solution (30 g, 1.0 wt.%), and HEA monomer (its mass was indicated in Fig. 3) were transferred into the different spray bottles, respectively, and sprayed evenly on the PVA1799 under mechanical stirring. During the spraying process, 2/3 of the initiator solutions and all HEA were evenly sprayed, and then the remaining initiator solutions were sprayed under consistent agitation. After completing the spraying process in 30 to 40 minutes, it was maintained at 40 ℃ for 3.5 h to conduct the grafting reaction. During this, the product was flipped every half hour. After the response, the product was redispersed with anhydrous ethanol, followed by filtering and washing 3 times, drying at 45 ℃, crushing, and sieving to gain the PVA1799-*g*-PHEA sample.

2.3. Measurement of grafting ratio

The grafting ratio (R_g, %) determines the graft polymerization level, indicating a mass percentage of grafted branches to grafted raw material. The R_g of PVA1799-*g*-PHEA was obtained by a weighing method and calculated using Eq. 1:

$$R_g(\%) = \frac{m_1 - m_2}{m_2} \times 100, \tag{1}$$

where m_1 and m_2 are the masses (g) of the dried PVA1799-*g*-PHEA obtained after the preparation process and the dried PVA1799 used in the grafting.

2.4. Fourier transform infrared (FTIR) analysis

To reveal the successful incorporation of PHEA branches on the PVA1799, the PVA1799 and PVA1799-*g*-PHEA were pressed into thin pellets with the KBr pellet technique and analyzed on the Nicolet Nexus 470 FTIR spectrophotometer (Thermo Electron Corporation, USA). The analysis was performed within 500 – 4000 cm^{-1} at a 4 cm^{-1} resolution.

2.5. Scanning electron microscopy (SEM) analysis

An S-4800 scanning electron microscope (SEM, Hitachi Limited, Japan) was adopted to collect the images of PVA1799 and PVA1799-*g*-PHEA. Before collection, coating the samples with gold layers was implemented.

2.6. Thermogravimetric (TG) analysis

The PVA1799 and PVA1799-*g*-PHEA samples were performed the TG analysis using a NETZSCH TG 209 F3 (NETZSCH-Gerätebau GmbH, Selb, Germany) at 35 – 600 °C and 10 °C/min with a flow rate of 200 m*l*/min for N_2.

2.7. Determination of adhesion

The adhesion of PVA samples to polyester/cotton fibers was investigated according to FZ/T 15001–2008 in China. The main steps of this method generally contain (a) making a size paste, (b) sizing the roving with the paste and drying it in the air to form the sized roving, and (c) tensile testing [16]. The PVA1799 or PVA1799-*g*-PHEA aqueous paste (1 wt.%, 900 mL) was prepared at 95 °C under consistent stirring. Then, the metal frame twining the polyester/cotton roving was submerged in the paste (700 mL) for 5 min, followed by air-drying to gain the sized roving. After being held at 20 °C and 65 % relative humidity (RH) for 1 d, the tensile testing of the sized roving was carried out with a YG026D electronic strength tester (Ningbo Textile Instrument Factory, China) at the drawing rate and clamping distance of 50 mm/min and 10 cm. The presented bonding force was the average of 20 tests, wherein any outlier data had been excluded.

2.8. Measurement of surface tension

After cooling down to room temperature, the surface tension of the residual paste (150 mL) was tested in duplicate on a DCAT 21 Full-Automatic Surface and Interface Tensiometer (Kono Industries Inc., Shanghai, China).

2.9. Measurement of light transmittance

Craig's method [17] was applied to measure the light transmittance of the paste (1 wt.%, the residual 50 mL) using a UV9600 spectrophotometer (Ruili Analytical Instrument Co., Ltd., Beijing, China) against a distilled water blank.

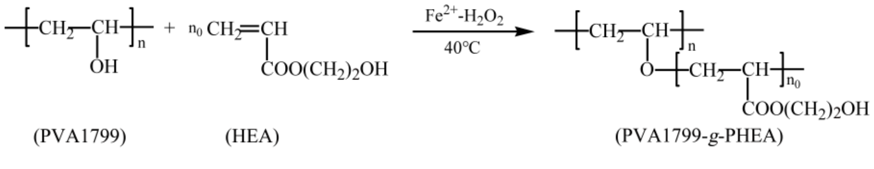

Fig. 1. Preparation of PVA1799-*g*-PHEA by the grafting of PVA1799 with HEA by the Fe^{2+}–H_2O_2 redox system

2.10. Preparation and determination of the film

A casting method presented in our previous study [18] was utilized to make the PVA1799 and PVA1799-*g*-PHEA films. The sample was mechanically stirred and thoroughly dissolved into distilled water at 95 °C to prepare the sample paste (6 wt.%, 400 mL), which was then poured onto a leveled glass plate covered with a polyester film (650 mm × 400 mm) and dried at 20 °C and 65 % RH to obtain the film. The film strips with the specifications of 200 mm × 10 mm, 100 mm × 20 mm, and 100 mm × 5 mm were prepared for the following determination.

The drawing tests of the strips (200 mm × 10 mm) were carried out on the YG026D tester at the drawing rate and clamping distance of 50 mm/min and 10 cm. The reported results were the mean values of 20 individual tests, wherein any outlier data had been excluded.

A YG731C instrument (Depp Textile Technology Co., Ltd., China) was utilized to measure the bending endurance (cycle) at a bending angle of 120° [19]. The strips with the specification of 100 mm × 5 mm were selected during the measurement.

Determination of the time to break the strip (100 mm × 20 mm) in distilled water at 80 °C was performed following the study [20]. The experiment involved adding a fixed mass of 1.0 g to one side of a film strip, and the strip was then half-immersed in the water. The strip broken time was read instantly. The presented result represented the mean value of 10 individual tests.

3. RESULTS AND DISCUSSION

3.1. FTIR analysis

The spectra of PVA1799 and PVA1799-*g*-PHEA samples were analyzed, as presented in Fig. 2. The peaks at about 1640 cm^{-1} and 1440 cm^{-1} in the spectra belonged to the O-H absorption peak in the combined water [21] and $-CH_2$ absorption peak [22], respectively.

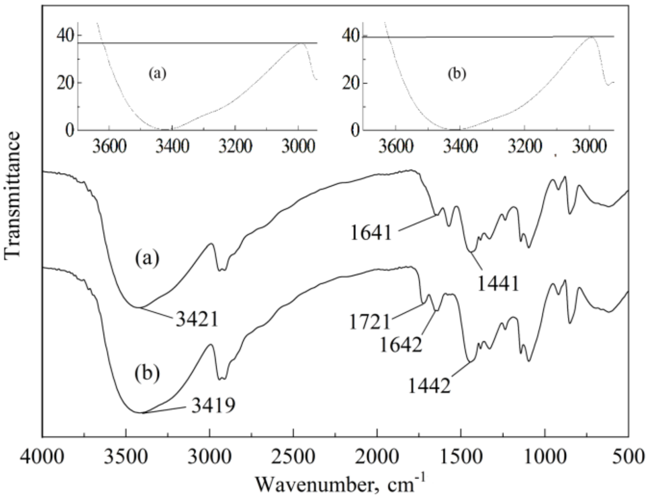

Fig. 2. FTIR spectra of (a) PVA1799; (b) PVA1799-*g*-PHEA (R_g = 7.3 %) samples

The band appeared at about 3420 cm^{-1}, indicating the characteristic peak of O–H [23, 24], and its intensity in the spectrum of PVA1799-*g*-PHEA was higher than the PVA1799 (as presented from the local enlarged drawing), which was due to the existence of O–H in the HEA units. Besides, one new peak at the 1721 cm^{-1} in the PVA1799-*g*-PHEA indicated the ester carbonyl absorption peak [25 – 27], revealing the successful incorporation of PHEA branches on the PVA1799.

3.2. Grafting ratio

Fig. 3 presents the grafting ratio (R_g) results of PVA1799-*g*-PHEA samples. The R_g gradually increased from 0 to 7.34 % with increasing the amounts of HEA from 0 g to 25 g. It indicated that the PVA1799-*g*-PHEA samples containing R_g values of 0 – 7.34 % could be successfully prepared via the grafting between PVA1799 (120 g) and HEA monomer (0 – 25 g) using the Fe^{2+}–H_2O_2 redox system in a dry process. With the increase in the amount of HEA, its concentration in the reaction system increased, which intensified the grafting reaction and formed more PHEA branches on the hydroxyls of PVA1799, inducing a gradual R_g value.

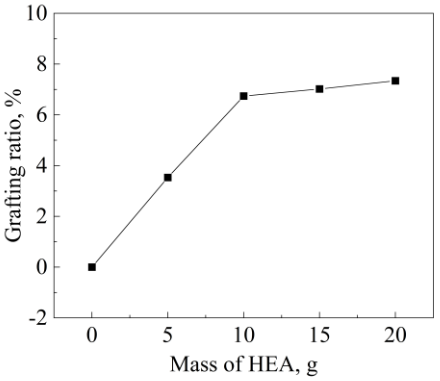

Fig. 3. The characterization of PVA1799-g-PHEA, i.e., grafting ratio

3.3. Surface morphology

SEM analysis of PVA1799 and PVA1799-*g*-PHEA was conducted to observe their surface morphology, as displayed in Fig. 4. As found, the PVA1799 (Fig. 4 a) used in this study showed a rough granule surface. It could be found in Fig. 4 b that the PVA1799-*g*-PHEA also possessed a rough granule surface and had no obvious difference from the surface of PVA1799. These implied that the graft polymerization of PVA1799 with HEA monomer by a dry process did not produce serious damage on the granule surface but retained the granular form of PVA1799.

3.4. TG analysis

The thermal degradation behaviors of PVA1799 and PVA1799-*g*-PHEA were estimated by TG analysis, as shown in Fig. 5. As seen, the PVA1799 and PVA1799-*g*-PHEA samples possessed the main three-stage and four-stage thermograms, respectively. The weight loss observed up to about 250 °C was attributed to the vaporization of water in both samples. The major weight losses of PVA1799-*g*-PHEA and PVA1799 were 56.8 % and 67.5 % in the temperature ranges of about 320 – 420 °C and 245 – 380 °C, respectively. The maximal decomposition temperatures of PVA1799-*g*-PHEA and PVA1799 were approximately 380 °C and 289 °C, respectively. These results revealed that the PHEA branches could alleviate the thermal degradation of PVA1799 and promote its thermal stability.

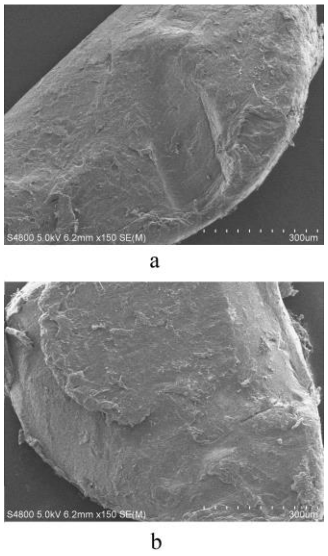

Fig. 4. a – SEM images of PVA1799, ×150; b – PVA1799-*g*-PHEA, R_g = 7.3 %, ×150

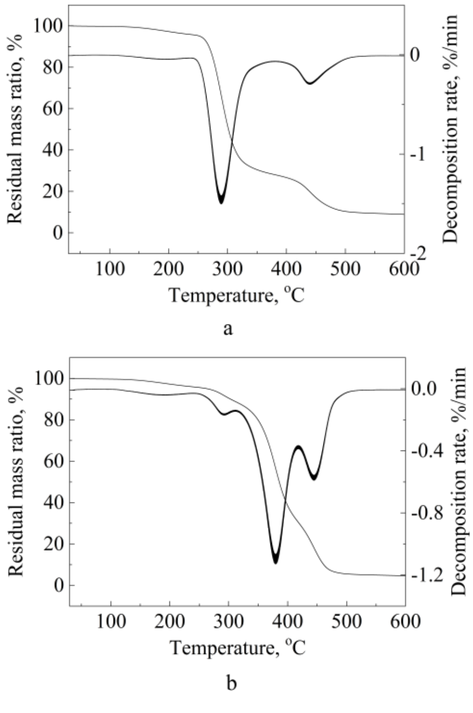

Fig. 5. a – TG-DTG of PVA1799; b – PVA1799-*g*-PHEA, R_g = 7.3 %

3.5. Effect of the grafted PHEA branches on the bonding forces

In warp sizing, it is well known that the polymer as a provisional adhesive enhances yarn strength [28]. Therefore, we investigated the effect of the grafted PHEA branches on the adhesion of PVA1799, as shown in Fig. 6. Compared to PVA1799, the bonding force of PVA1799-*g*-PHEA to polyester/cotton roving was significantly enhanced. The bonding force of PVA1799-*g*-PHEA depended on the R_g, which gradually increased with increasing the R_g from 3.53 % to 7.34 %. These findings concluded that incorporating PHEA branches improved the adhesion of PVA1799 to fibers, and a greater improvement in the adhesion was exhibited as more PHEA branches were grafted onto PVA1799.

During the air-drying of the sized roving, the PVA sample paste existing among the fibers within the roving converts into PVA adhesive layers. Adhesive failure may occur under external forces during the tensile testing of sized roving. There are two types of adhesive failures based on the location of the fracture: cohesive and interfacial failures [29]. The former primarily happens within the layer matrix, while the latter occurs at the layer/fiber interfaces. It is crucial for enhancing adhesion by reducing the occurrence of adhesive failures.

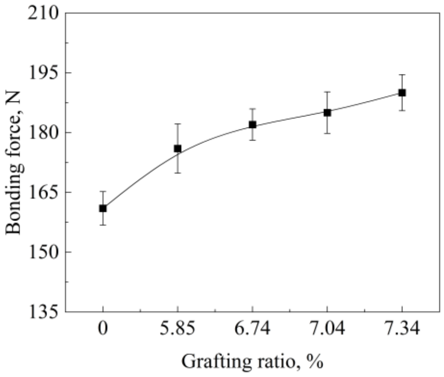

Fig. 6. Influence of grafting ratio on the adhesion of PVA1799 to polyester/cotton fibers

As proved, the paste with a low surface tension wets and spreads the fiber surface strongly, favoring bonding to fibers [30]. Therefore, to better understand the superior bonding forces for PVA1799-*g*-PHEA, it is essential to focus on surface tension. The surface tension of PVA1799-*g*-PHEA and control PVA1799 pastes was tested, as presented in Fig. 7.

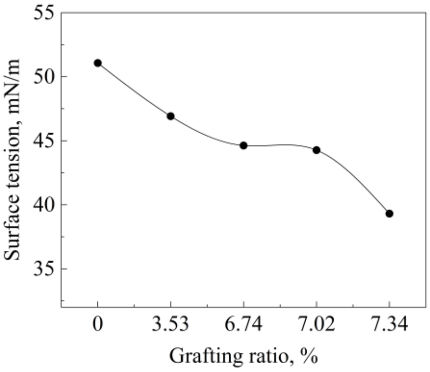

Fig. 7. Effect of grafting ratio on surface tension of PVA1799 paste

It indicated that the amphipathic PHEA branches exerted an effective effect on reducing the tension, which was necessary to improve the surface activity of PVA1799. Interfacial defects around outspreaded areas will occur due to poor wetting and outspreading, resulting in noticeable damage to bonding. [31]. Consequently, incorporating amphipathic PHEA branches might acquire stronger wetting and spreading abilities to abate the interfacial failure, thereby facilitating the bonding to polyester/cotton fibers.

Furthermore, the graft polymerization of PVA1799 with the HEA monomer introduces grafted PHEA branches onto the PVA1799. These branches function as wedges, preventing the ordered arrangement of PVA1799 chains and reducing the association of PVA hydroxyls. This process plasticizes the PVA adhesive layers, effectively decreasing the likelihood of cohesive failure and enhancing adhesion.

Adhesives can generate chemical forces between the bonded materials, primarily through hydrogen bonds and van der Waals forces [28]. When the adhesive surface is near the bonded material surface, chemical forces can develop at the interfaces due to the recombination of radicals on their surfaces [32]. These chemical forces at the interfaces significantly influence adhesive bonding strength to the bonded material [33]. Many polar hydroxyls exist on the cotton and PVA1799-*g*-PHEA chains (in the HEA units and PVA molecules). The chemical interactions between the hydroxyl groups at the interfaces of adhesive layers and cotton fibers will enhance the interaction at the interface, thereby improving adhesion to cotton fibers. The primary interactions that occur are van der Waals forces and hydrogen bonds. The ester groups in the HEA units of PVA1799-*g*-PHEA are similar to those in polyester, promoting van der Waals forces that enhance the bonding of PVA1799-*g*-PHEA to polyester fibers.

Additionally, the paste wetting and spreading of the sizing agent are also related to its water dispersibility. Usually, the higher the water dispersibility, the better the wetting and spreading. Water dispersibility is commonly assessed by determining the light transmittance of the paste. The light transmittance results of PVA1799-*g*-PHEA and control PVA1799 (grafting ratio = 0 %) pastes are presented in Fig. 8.

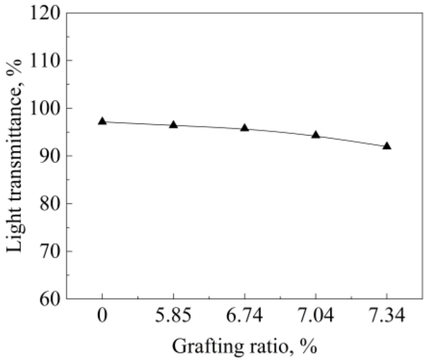

Fig. 8. Effect of grafting ratio on light transmittance of PVA1799 paste

As seen, the light transmittance of PVA1799-*g*-PHEA paste was slightly lower than that of control PVA1799 paste, which meant that introducing the PHEA branches did not lead to an obvious decrease in the light transmittance, whereas just caused a slight decrease. Therefore, introducing the PHEA branches had no obvious effect on the water dispersibility of PVA1799, which revealed that water dispersibility showed a subtle influence on the adhesion of PVA1799-*g*-PHEA.

As a result, grafting PHEA branches onto PVA1799 significantly improves its bonding force with polyester/cotton roving compared to unmodified PVA1799. As the R_g increases, the number of grafted PHEA branches rises, positively affecting wetting, spreading, internal plasticization, and chemical interactions, which in turn gradually increases the bonding force.

3.6. Effect on film properties

The warp sizing process creates a protective film on the warp surface, enhancing abrasion resistance and facilitating smooth weaving [11]. Therefore, investigating the film properties of PVA1799-*g*-PHEA samples is essential to ensure their strength and toughness against mechanical actions.

Fig. 9 illustrate how the grafting ratio affects the tensile properties: tensile strength and breaking elongation of the PVA1799 film.

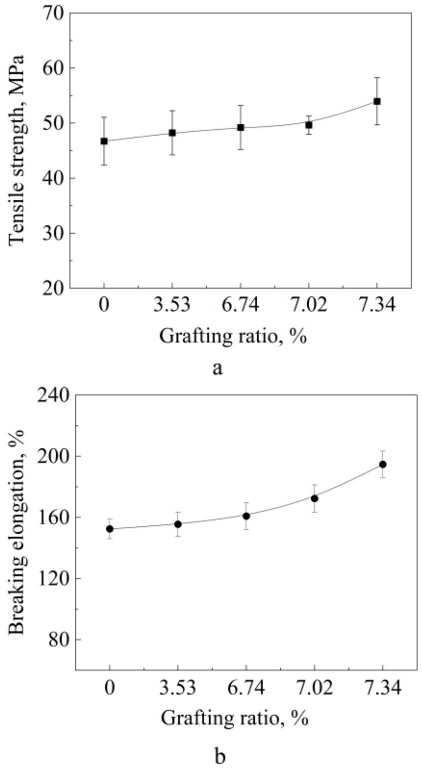

Fig. 9. a – effect of grafting ratio on the tensile strength; b – breaking elongation of the film (grafting ratio = 0 indicates the PVA1799 film)

It can be observed that the films produced from PVA1799-*g*-PHEA pastes exhibit greater elongation and slightly higher strength compared to those made from the PVA1799 paste. The PVA1799-*g*-PHEA possessed a gradually increased film elongation and a slightly increased film strength as the grafting ratio rose. The significantly increased elongations of PVA1799-*g*-PHEA (grafting ratio ≥ 7.02 %) films were displayed compared to the PVA1799 film. The PVA1799-*g*-PHEA (grafting ratio = 7.34 %) film achieved the highest elongation of 194.7 % compared to that (152.4 %) for PVA1799 film. These observations indicated that the PVA1799-*g*-PHEA films were more stretchable than the PVA1799 film, and the grafted PHEA branches could promote the tensile properties of the PVA1799 film. Undoubtedly, the PVA1799-*g*-PHEA film with greater extendibility is more effective than the PVA1799 film in protecting warps during the weaving process. In addition, Table 1 displays how the grafting ratio affects the bending endurance of the film. It could be found that both PVA1799-*g*-PHEA and PVA1799 films possessed bending endurances of higher than 20000 cycles, which revealed that the PVA1799-*g*-PHEA film still had excellent bending endurance. The excellent bending endurance made the film exhibit strong flexibility, favoring the weaving.

Table 1. Effect of grafting ratio on the bending endurance of PVA film

PVA samples	Grafting ratio, %	Bending endurance, cycles
PVA1799	0	>20000
PVA1799-*g*-PHEA	3.53	>20000
	6.74	>20000
	7.04	>20000
	7.34	>20000

The introduced PHEA branches act as wedges by their steric hindrance to interfere with the ordered arrangement of PVA1799 chains, lessen the association between PVA hydroxyl groups, and increase the distance between PVA chains, consequently inducing an internal plasticization to the PVA film, thereby imparting a higher breaking elongation to the PVA1799-*g*-PHEA film. In addition, the hydroxyls existing in the PVA chains and PHEA branches can associate to form hydrogen bonds, which may explain why the introduction of PHEA branches results in a slight increase in tensile strength.

Besides, the study also evaluated how the grafting ratio affected the time it took for the PVA film to break in hot water, aiming to determine whether the introduction of PHEA branches improved the desizability of PVA1799. The results in Fig. 10 showed that PVA1799-*g*-PHEA films broke faster than the PVA1799 film (grafting ratio = 0 %).

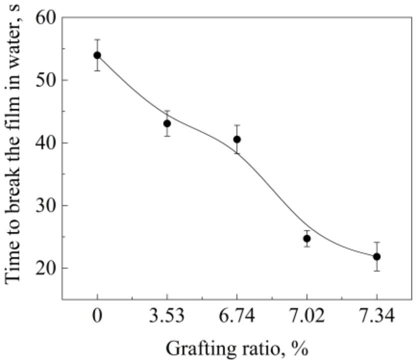

Fig. 10. Effect of grafting ratio on the time to break the PVA film in hot water

This implied that PHEA branches decreased the film's time to break in distilled water at 80 °C. The results showed that there was an inverse relationship between time and the R_g; specifically, as the R_g increased, the time required decreased. The PHEA branches increase the distance between PVA chains due to steric hindrance and hydroxyl groups from the HEA units. This change promotes water penetration into the PVA material, resulting in the rapid swelling of the PVA film when immersed in water. As a result, a decreased time is found, indicating that desizing PVA from the warps is easier, suggesting that the PHEA branches help accelerate this process.

4. CONCLUSIONS

The previous results indicated that adding synthetic PHEA branches to the PVA1799 effectively improved its sizing properties, particularly the adhesion to polyester/cotton fibers and film characteristics. Compared to the control PVA1799, the PVA1799-*g*-PHEA, which had a grafting ratio ranging from 3.53 % to 7.34 %, demonstrated significantly stronger bonding forces with polyester/cotton roving. This suggested that the incorporation of PHEA branches markedly enhanced the adhesion. The enhancement is mainly attributed to the improvement of wetting and spreading arising from the lessened surface tension, the induced internal plasticization, and the produced chemical forces (van der Waals forces and hydrogen bonds) after incorporating the PHEA branches. The PVA1799-PHEA film exhibited greater breaking elongation and a slight increase in tensile strength compared to the PVA1799 film. This indicated that the PHEA branches had positively influenced the tensile properties of the PVA1799 film. In addition, both PVA1799-*g*-PHEA and PVA1799 films had excellent bending endurance, and the former broke in hot water in a shorter time than the latter, suggesting that the introduction of PHEA branches favored promoting the desizing of PVA from warp yarns. As the grafting ratio increased from 3.53 % to 7.34 %, there was a corresponding increase in bonding forces and film elongation and a decreased time required. Based on these results, PVA1799-*g*-PHEA with a grafting ratio of 7.34 % as a new PVA-based sizing agent showed potential application in the sizing of polyester/cotton warps.

Acknowledgments

This work was supported by the University Youth Talent Support Program of Anhui Province (No. gxyq2022024), the Research Project of Anhui Polytechnic University (No. Xjky2022081 and No. HX202303105), and China.

REFERENCES

1. **Zhou, Y.Y.** Theory of Textile Warp Sizes. China Textile & Apparel Press, Beijing, 2004.
2. **Zhu, Z.F.** Chemistry in Textile Engineering. Donghua University Press Co. Ltd, Shanghai, 2010.
3. **Zhu, Z.F., Song, Y.Z., Xu, Z.Z., Li, W., Zhang, C.H.** Introduction of Octenylsuccinate and Carboxymethyl onto Starch for Strong Bonding to Fiber and Easy Removal from Sized Yarn *Carbohydrate Polymers* 269 2021: pp 118249. https://doi.org/10.1016/j.carbpol.2021.118249
4. **Djordjevic, S., Kovacevic, S., Djordjevic, D., Konstantinovic, S.** Sizing Process of Cotton Yarn by Size from A Copolymer of Methacrylic Acid and Hydrolyzed Potato Starch *Textile Research Journal* 89 2019: pp. 3457 – 3465. https://doi.org/10.1177/0040517518813628
5. **Bhattacharyya, R., Kumar, R., Bandyopadhyay, K.K., Saha, M., Chawla, G., Saha, J. K., Patra, A.K.**

Preparation of Novel Biodegradable Starch/Poly(Vinyl Alcohol)/Bentonite Grafted Polymeric Films for Fertilizer Encapsulation *Carbohydrate Polymers* 259 2021: pp. 117679. https://doi.org/10.1016/j.carbpol.2021.117679

6. **Wang, Y.T., Meng, Y., Ji, Z., Meng, X.M., Song, X.M., Lu, P., Chen, F.S.** Bioinspired Colored Degradable Starch-Based Films with Excellent Tensile Strength *Industrial Crops and Product* 167 2021: pp. 113525. https://doi.org/10.1016/j.indcrop.2021.113525
7. **Saari, R.A., Maeno, R., Marujiwat, W., Nasri, M.S., Matsumura, K., Yamaguchi, M.** Modification of Poly(Vinyl Alcohol) Fibers with Lithium Bromide *Polymer* 213 2020: pp. 123193. https://doi.org/10.1016/j.polymer.2020.123193
8. **Gaaz, T.S., Sulong, A.B., Akhtar, M.N., Kadhum, A.A.H., Mohamad, A.B., Al-Amiery, A.A.** Properties and Applications of Polyvinyl Alcohol, Halloysite Nanotubes and Their Nanocomposites *Molecules* 20 2015: pp. 22833 – 22847. https://doi.org/10.3390/molecules201219884
9. **Qiu, K.Y., Netravali, A.N.** A Composting Study of Membrane-like Polyvinyl Alcohol Based Resins and Nanocomposites *Journal of Polymers and the Environment* 21 2013: pp. 658 – 674. https://doi.org/10.1007/s10924-013-0584-0
10. **Kim, D.H., Park, M.S., Choi, Y.J., Lee, K.B., Kim, J.H.** Synthesis of PVA-*g*-POEM Graft Copolymers and Their Use in Highly Permeable Thin Film Composite Membranes *Chemical Engineering Journal* 346 2018: pp. 739 – 747. https://doi.org/10.1016/j.cej.2018.04.036
11. **Maqsood, M., Khan, M.I., Shaker, K., Umair, M., Nawab, Y.** Recycling of Warp Size Materials and Comparison of Yarn Mechanical Properties Sized with Recycled Materials and Virgin Materials *The Journal of The Textile Institute* 108 2017: pp. 84 – 88. https://doi.org/10.1080/00405000.2016.1153875
12. **Wang, X., Huang, L.X., Zhang, C.H., Deng, Y.J., Xie, P.J., Liu, L.J., Cheng, J.** Research Advances in Chemical Modifications of Starch for Hydrophobicity and Its Applications: A Review *Carbohydrate Polymers* 240 2020: pp. 116292. https://doi.org/10.1016/j.carbpol.2020.116292
13. **Li, W., Wu, L.J., Zhu, Z.F., Zhang, Z.Q., Liu, Q., Lu, Y.H., Ke, H.Z.** Incorporation of Poly(Sodium Allyl Sulfonate) Branches on Corn Starch Chains for Enhancing Its Sizing Properties: Viscosity Stability, Adhesion, Film Properties and Desizability *International Journal of Biological Macromolecules* 166 2021: pp. 1460 – 1470. https://doi.org/10.1016/j.ijbiomac.2020.11.025
14. **Kovacevic, S., Schwarz, I., Djordjevic, S., Djordjevic, D.** Synthetized Potato Starch – A New Eco Sizing Agent for Cotton Yarns *Polymers* 11 2019: pp. 908. https://doi.org/10.3390/polym11050908
15. **Wang, W.D., Wang, Q., Wang, P.** Hydrophobic Modification of Starch via Enzymatic Grafting Polymerization of Fluorinated Vinyl Monomer *Carbohydrate Research* 549 2025: pp. 109376. https://doi.org/10.1016/j.carres.2025.109376
16. **Li, W., Wu, J., Zhang, Z.Q., Wu, L.J., Lu, Y.H.** Investigation on the Synthesis Process of Bromoisobutyryl Esterified Starch and Its Sizing Properties: Viscosity Stability, Adhesion and Film Properties *Polymers* 11 2019: pp. 1936. https://doi.org/10.3390/polym11121936
17. **Craig, S.A.S., Maningat, C.C., Seib, P.A., Hoseney, R.C.** Starch Paste Clarity *Cereal Chemistry* 66 1989: pp. 173 – 182. https://doi.org/10.1021/cen-v065n014.p037
18. **Li, W., Cheng, X.D., Wang, Y.F., Xu, Z.Z., Ke, H.Z.** Quaternization-Butyrylation to Improve the Viscosity Stability, Adhesion to Fibers, Film Properties and Desizability of Starch for Warp Sizing *International Journal of Biological Macromolecules* 204 2022: pp. 500 – 509. https://doi.org/10.1016/j.ijbiomac.2022.02.021
19. **Li, W., Cheng, X.D., Xu, Z.Z., Ruan, F.T., Yan, H.Q.** Modification of Biological Starch Macromolecule with Phosphate and Dimethylammonium Chloride Acyloxylate Substituents Confers Good Desizability, Film Properties, Paste Stability and Adhesion *International Journal of Biological Macromolecules* 258 2024: pp. 128862. https://doi.org/10.1016/j.ijbiomac.2023.128862
20. **Li, W., Xu, Z.Z., Wang, Z.Q., Liu, X.H., Li, C.L., Ruan, F.T.** Double Etherification of Corn Starch to Improve Its Adhesion to Cotton and Polyester Fibers *International Journal of Adhesion and Adhesives* 84 2018: pp. 101 – 107. https://doi.org/10.1016/j.ijadhadh.2018.03.001
21. **Li, W., Zhang, Z.Q., Zhang, X., Wang, Y.F., Ruan, F.T., Xing, J.** Synthesis of Grafted Bromoisobutyryl Esterified Starch using Electron Transfer Atom Transfer Radical Polymerization Method with High-Performance Adhesion and Film Properties *International Journal of Biological Macromolecules* 266 2024: pp. 131421. https://doi.org/10.1016/j.ijbiomac.2024.131421
22. **Li, W., Wu, L.J., Xu, Z.Z., Liu, Z.** Adhesion-to-Fibers and Film Properties of Etherified-Oxidized Cassava Starch/Polyvinyl Alcohol Blends *Iranian Polymer Journal* 29 2020: pp. 331 – 339. https://doi.org/10.1007/s13726-020-00798-5
23. **Li, W., Liu, Q., Cheng, X.D., Xu, Z.Z.** Amphipathic Combination of Poly(Sodium Allyl Sulfonate) and Poly(Ethyl Acrylate) on Starch for Strong Adhesion to Cotton Fibers and Film Properties *Industrial Crops and Product* 177 2022: pp. 114461. https://doi.org/10.1016/j.indcrop.2021.114461
24. **Hong, W., Meng, M.W., Xie, J.L., Gao, D.D., Xian, M.N., Wen, S., Huang, S.Y., Kang, C.Y.** Properties and Thermal Analysis Study of Modified Polyvinyl Acetate (PVA) Adhesive *Journal of Adhesion Science and Technology* 32 2018: pp. 1 – 15. https://doi.org/10.1080/01694243.2018.1465687
25. **Wang, L.L., Shen, J.N., Men, Y.J., Wu, Y., Peng, Q.H., Wang, X.L., Yang, R., Mahmood, K., Liu, Z.P.** Corn Starch-Based Graft Copolymers Prepared via ATRP at the Molecular Level *Polymer Chemistry* 6 2015: pp. 3480 – 3488. https://doi.org/10.1039/c5py00184f
26. **Yoshimura, T., Yoshimura, R., Seki, C., Fujioka, R.** Synthesis and Characterization of Biodegradable Hydrogels Based on Starch and Succinic Anhydride *Carbohydrate Polymers* 64 2006: pp. 345 —349. https://doi.org/10.1016/j.carbpol.2005.12.023
27. **Chang, P.R., Qian, D.Y., Anderson, D.P., Ma, X.F.** Preparation and Properties of the Succinic Ester of Porous Starch *Carbohydrate Polymers* 88l 2012: pp. 604 —608. https://doi.org/10.1016/j.carbpol.2012.01.001
28. **Li, W., Zhang, Z.Q., Wu, L.J., Liu, Q., Cheng, X.D., Xu, Z.Z.** Investigating the relationship between structure of

itaconylated starch and its sizing properties: Viscosity stability, adhesion and film properties for wool warp sizing *International Journal of Biological Macromolecules* 181 2021: pp. 291 – 300. https://doi.org/10.1016/j.ijbiomac.2021.03.143

29. **Ebnesajjad, S., Ebnesajjad, C.F.** Surface Treatment of Materials for Adhesive Bonding. Elsevier Inc, Netherlands, 2014.
30. **Li, W., Zhang, Z.Q., Wu, L.J, Zhu, Z.F., Xu, Z.Z.** Improving the Adhesion-to-Fibers and Film Properties of Corn Starch by Starch Sulfo-itaconation for a Better Application in Warp Sizing *Polymer Testing* 98 2021: pp. 107194. https://doi.org/10.1016/j.polymertesting.2021.107194
31. **Wu, S.H.** Polymer Interface and Adhesion. Marcel Dekker, New York, 1982.
32. **Mutsuda, M., Komada, H.** Direct Bonding between Poly (Oxy-2,6-dimethyl-1,4-phenylene) and Rubber with Radicals *Journal of Applied Polymer Science* 95 2005: pp. 53 – 59. https://doi.org/10.1002/app.20803
33. **Chai, S.Y., Liu, J., Hou, D.S., Wang, P.** Molecular Insights into the Interfacial Adhesion Mechanism between Carbon Nanotubes and Epoxy Resin *RSC Advances* 13 2023: pp. 30915. https://doi.org/10.1039/D3RA05749F