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Influence of Lawsone Dye on Surface Properties of Polyethylene Terephthalate Fabric

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Abstract: To enhance the hydrophilicity and antistatic properties of the polyethylene terephthalate (PET) fabric, the lawsone dye was employed in dyeing the PET fabric. It was dissolved in ethanol/deionized water mixture and deionized water separately, forming different lawsone dye solutions (LDSs). The study investigated how the compounds in the LDS improve the surface properties and color durability of the PET fabric, resulting in increased dye uptake. An infrared dyeing machine was utilized to expedite the reactions between the lawsone dye and the PET fabric. Additionally, the chemical composition of the dyed PET fabric was verified using techniques such as Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and ultraviolet-visible (UV-Vis) spectrophotometry. The *K/S* value was measured to assess color durability. After dyeing, the PET fabric exhibited high hydrophilicity which improved the hygroscopicity of the PET fabric and thus the conductivity of the PET fabric surface increased, thereby providing an antistatic effect.

Keywords: polyethylene terephthalate (PET); lawsone; hydrophilicity; antistatic
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0 Introduction

Natural dyes possess color since they contain a chromophoric structure consisting of an extended conjugated system[1]. Due to their environmental friendliness, good biodegradability and non-toxic nature, natural dyes have gained significant attention in the fields of textiles[2-4]. Henna has astringent, moisturizing and antimicrobial properties in traditional medicine and cosmetics[5]. Lawsone, derived from henna, is utilized to color textiles as a natural plant-based dye[6-9]. Lawsone is a natural compound belonging to the naphthoquinone family with a structure that consists of a bonded ring system with a hydroxyl group (—OH) attached to the aromatic rings and double bonds of the carbonyl group ($C=O$). This structure contributes to its color and reactivity.

By understanding the specific chemical structures and active groups in natural dyes, researchers can adapt dye formulations to promote effective bonding with the fabric and improve its surface energy[10-11]. Moreover, solvent systems can contribute to the polarity of a molecule by affecting the electronegativity and arrangement of atoms and indirectly influence the occurrence of hydrogen bonding. Since solvent systems are affected by the type and properties of the solvent, selecting the proper solvent is crucial.

The selection of solvents for extraction depends on the specific chemicals being extracted, and the factors such as solubility, polarity and concentration of the chemicals should be considered. Ethanol, a solvent possessing polar protic characteristics, exhibits selectivity in extracting compounds from different sources[12]. The water molecule is highly polar due to the significant difference in electronegativity between the oxygen and hydrogen atoms[13]. Due to their polarity, ethanol and water can dissolve polar molecules, create hydrogen bonds, and have higher boiling points than many small nonpolar compounds[14-15]. Moreover, their inherent polarity allows them to blend in varying ratios, producing homogeneous mixtures.

The polyethylene terephthalate (PET) fabric is commonly hydrophobic and its relatively low surface energy limits its ability to absorb moisture. Surface modification can improve the performance of the PET fabric[16-18]. The intermolecular forces acting between the natural dye and the PET fabric during the dyeing process could enhance the fabric's ability to absorb water and increase dye uptake, along with other beneficial properties for future applications.

As a result, applying lawsone dye to the surface of the PET fabric is expected to introduce hydrophilicity, there by improving the moisture absorption of the PET fabric and reducing static electricity on it. In this paper, the hydrophilicity and antistatic properties of the PET fabric are investigated before and after lawsone dyeing.

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The chemical composition and surface morphology are analyzed to confirm the presence of lawsone dye on the PET fabric. In addition, the effect of the solvent system on color durability is also investigated.

1 Materials and Methods

1.1 Materials

The PET fabric (150 g/m^2) was purchased from Ningbo Hengda Printing and Dyeing Co., Ltd. The lawsone dye powder derived from the henna plant was from Sudan. Ethanol and other reagents were provided by Aladdin Industrial Corporation, China. All reagents were used without further purification.

1.2 Extraction of lawsone dye

The lawsone dye powder was dried until it reached a constant mass. Then, the lawsone dye powder (25 g) was taken and dissolved in a mixed solvent (1 L) composed of ethanol and deionized water in a volume ratio of 1∶9. For comparison, deionized water was used as the other solvent. After 24 h of complete dissolution, each sample was filtered, and the lawsone dye solution (LDS) was obtained. The color of the LDS varied due to the lawsone state in the solvent. The LDS prepared with the mixed solvent (LDS-E) is brown, while the LDS prepared with deionized water (LDS-W) displays a reddish-orange color.

1.3 Dyeing of PET fabric

The PET fabric was dyed using an infrared dyeing machine (Daelim Starlet Co., Ltd., the Republic of Korea). Both of the LDSs applied to the PET fabric had a liquor ratio of 30 ∶ 1. The different dye temperatures (100, 110, 120 and 130 ℃) were applied. Subsequently, the dyed PET fabric was washed with deionized water. After dyeing, the PET fabric dyed with LDS-E was named the PET-E fabric, and the PET fabric dyed with LDS-W was named the PET-W fabric.

1.4 Absorption spectrum of LDS

The LDS was prepared at different mass concentrations, and the absorption spectrum was obtained using an ultraviolet-visible (UV-Vis) spectrophotometer (UV-3600, Shimadzu, Japan). The wavelength range extended from 200 nm to 400 nm, and the optical data were obtained.

1.5 *K/S* value and wash fastness of dyed PET fabric

The *K/S* value was determined using a spectrophotometer (Datacolor 600, Datacolor Co., USA). The artificial daylight with a color temperature of 6 500 K at a 10° viewing angle was used. Five different positions on the same dyed PET fabric were selected to test the amount of light reflected and absorbed by the sample. Meanwhile, the wash fastness, specifically colorfastness to washing, was measured in an instrument (SW-24A, Wenzhou Darong Textile Instrument Co., Ltd., China), referring to AATCC 8-2008 standard (Colorfastness to Crocking: AATCC Crockmeter Method).

1.6 Moisture regain of PET fabric

A PET fabric sample was placed in an oven at 105 ℃ for 2 h and dried to a constant mass. Then the sample was balanced for 24 h in the environment at a temperature of 20 ℃ and a relative humidity of 65%. The moisture regain R_{moi} of the sample was calculated as

$$R_{\mathrm{moi}} = \frac{m_2 - m_1}{m_1} \times 100\%,$$

where m_1 is the mass of the dried sample; m_2 is the mass of the sample after humidity control balance.

1.7 Antistatic property of dyed PET fabric

An electrostatic induction fabric tester (Electromechanical Technology Co., Ltd., China) was utilized to assess the electrostatic characteristics of the PET fabric. The PET fabric was sized with the dimension of 45 mm×45 mm.

1.8 Wettability of dyed PET fabric

The water contact angle (WCA) test was used to measure the wettability of the fabric through a drop shape analyzer (DSA30S, KRUSS GmbH, Germany). Deionized water was dropped on the fabric surface at five different locations to measure the WCA.

1.9 Characterization

The functional groups of the PET fabric were characterized by Fourier transform infrared (FTIR) spectroscopy using an FTIR spectrometer (PerkinElmer, USA) over a wavenumber range of 4 000–400 cm^{-1} at a resolution of 4 cm^{-1}. The crystal structures of the PET fabric were investigated by X-ray diffraction (XRD) (D2 Phaser, Bruker, Germany) in the reflection mode. The thermal degradation and stability of the PET fabric were measured by a thermal gravimetric analysis (TGA) instrument (Netzsch, Germany) under the nitrogen atmosphere. The surface morphology of the PET fabric was observed using a scanning electron microscope (SEM) (TM-1000, Hitachi, Japan).

2 Results and Discussion

2.1 UV-Vis absorption behavior of LDS

Figure 1 shows differences in UV-Vis absorption of LDS-E and LDS-W, indicating that the arrangement of atoms within the dye molecules varies in different solvents. The maximum absorption peak of LDS-E appears at 269 nm, and that of LDS-W appears at 275 nm. The maximum absorption peaks show different levels when LDS is at different mass concentrations. At a higher mass concentration of 20 mg/L, LDS-E shows a higher absorbance value compared to LDS-W. Conversely, at a lower mass concentration of 4 mg/L, LDS-W displays a higher absorbance value than LDS-E. This shift can be attributed to the influence of solvent polarity and hydrogen bonding on the UV-Vis absorption of LDS. These factors alter the electron cloud distribution of the molecules in LDS, modify their energy level structures, and affect intermolecular interactions, thereby impacting the position and intensity of the absorption peaks.

The durable coloration of both the PET-E fabric and the PET-W fabric, along with the variations in color shades (Fig. 2 (a)), can be attributed to the solvent system. During the dyeing process, as lawsone molecules diffuse into the PET fabric, the conjugated carbonyl group and the hydroxyl group attached to the aromatic rings contribute to the formation of molecular orbitals through their hybrid orbital states (Fig. 2 (b)). The different colors of lawsone in various solvent systems stem from the changes in its molecular structure and interactions with the solvent, which alter the wavelength of the absorbed light and thus the observed color.

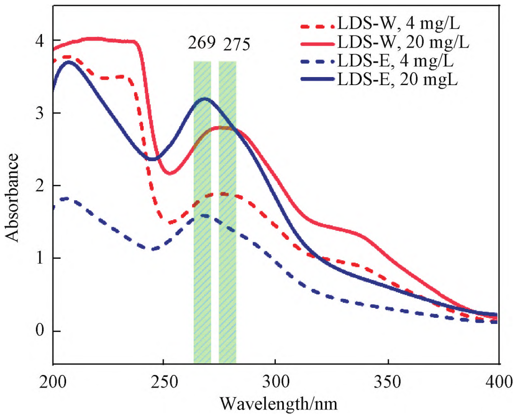
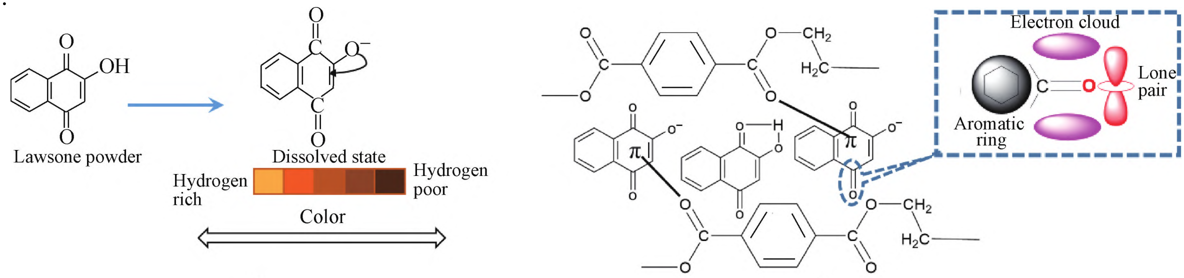


Fig. 1 UV-Vis spectra of LDSs at different mass concentrations



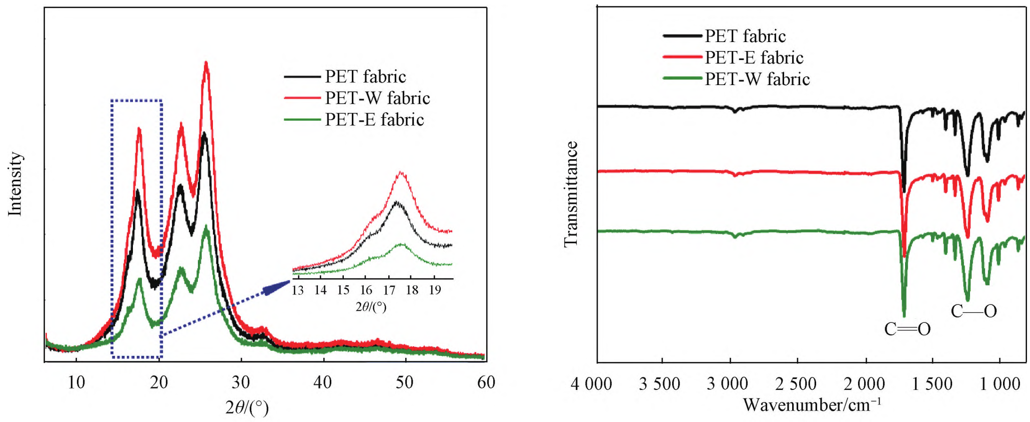
(a) (b)

Fig. 2 Lawsone molecular structures in different states: (a) lawsone powder dissolved in solvents; (b) lawsone dyed in PET fabric

2.2 XRD and FTIR analyses

The XRD patterns of the PET fabric, the PET-W fabric and the PET-E fabric are shown in Fig. 3(a). The PET fabric exhibits a medium peak, which matches the phase lattice parameter. After dyeing with LDS, the intensity of the peaks corresponding to the PET-W fabric increased, while the intensity of the peaks associated with the PET-E fabric decreased. The state of lawsone might influence the PET fabric surface's lattice and geometry, which could also alter the crystal structure and packing of polymer chains, leading to various XRD patterns.

The FTIR spectra of PET fabrics are shown in Fig. 3(b). The absorption peaks of the PET fabric at 1 240 cm^{-1} and 1 708 cm^{-1} correspond to the stretching vibrations of the C—O and C═O bonds[17], respectively. These vibrations are directly related to the stretching of ester groups. The FTIR results indicate that no new chemical bonds are formed after dyeing with LDS.



(a) (b)

Fig. 3 Characterization of PET fabric before and after dyeing: (a) XRD; (b) FTIR

2.3 Effects of LDS solvent system on PET fabric

The structure of the carbon atom and the electronegativity of nearby atoms are two factors that affect the C 1s binding energy. In Fig. 4(a), the C 1s peak at 288.6 eV corresponds to the C═O bonds, and two peaks at 286.2 eV and 284.6 eV correspond to the C—O and C—H bonds[19], respectively. After the dyeing process, in the PET-W fabric, the C 1s peak related to the C ═O bonds appears at 288.4 eV and becomes broader (Fig. 4(b)). Furthermore, there is a slight change in the C 1s peaks corresponding to the C—O and C—H bonds. Figure 4(c) shows a decrease in the binding energy of C 1s associated with the C═O bonds in the PET-E fabric and the peak becomes broader. Compared to the PET fabric and the PET-W fabric, in the PET-E fabric's C 1s spectra, the peak related to the C—O bonds is broader and higher, while the peak related to the C—H bonds shows a decrease in height. These changes indicate that the lawsone dye effectively modified the surface structure of the PET fabric.

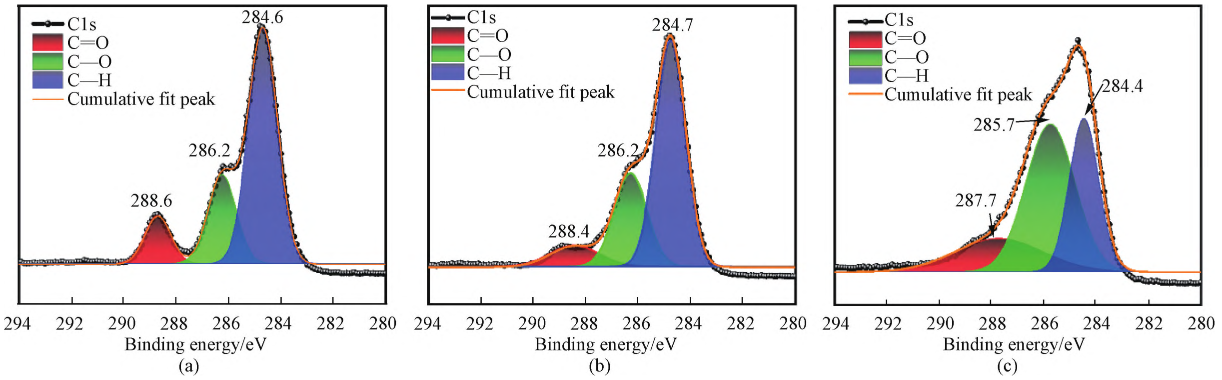


Fig. 4 XPS survey spectra: (a) C 1s of PET fabric; (b) C 1s of PET-W fabric; (c) C 1s of PET-E fabric

2.4 Thermal stability of PET fabric after dyeing

Figure 5 shows that the thermal stability of the PET fabric remains almost unchanged before and after dyeing, as evidenced by a slight difference in mass loss during TGA. Additionally, XPS analysis (Fig. 6) supports the presence of intermolecular forces as the primary interaction between lawsone dye and the PET fabric. This implies that the successful diffusion of LDS molecules into the PET fabric is primarily driven by intermolecular interactions rather than the formation of covalent bonds.

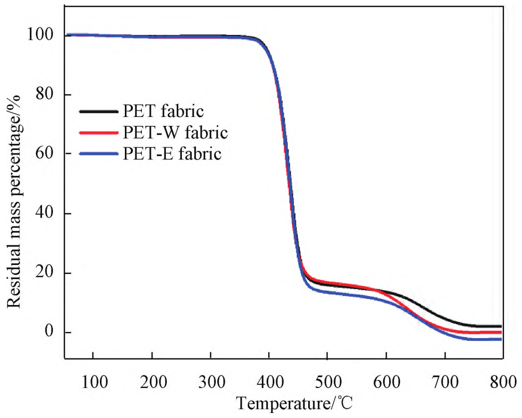


Fig. 5 Thermal stability of PET fabric before and after dyeing

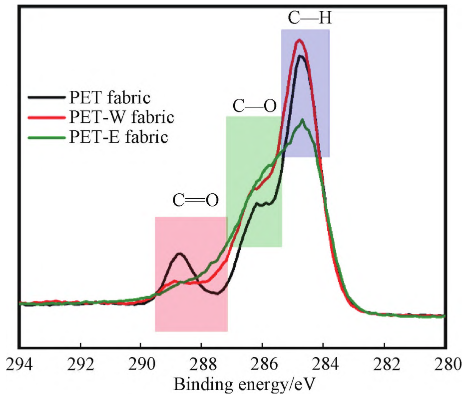


Fig. 6 C 1s XPS survey spectra of PET fabric before and after dyeing

2.5 Coloring durability

The *K/S* value refers to a measure of the color depth and dye absorption efficiency for a dyed fabric. It indicates how effectively a given concentration of dye produces a durable color with a considerable depth of shade. Figure 7(a) indicates that the *K/S* value of the PET-E fabric and the PET-W fabric positively correlated with the dyeing temperature. This is due to the significant influence of temperature on dye absorption and color retention during the dyeing process[16]. Figure 7(b) displays the results of measuring the *K/S* value with different wash cycles. The PET-E fabric shows a higher *K/S* value, while the PET-W fabric shows a lower *K/S* value. However, both samples demonstrate excellent wash fastness.

The elevated *K/S* values of the PET-E fabric suggest that the lawsone dye exhibits greater affinity and adherence. Furthermore, the changes in surface energy and morphology may impact the interaction between the lawsone dye and the PET fabric, thereby influencing the dye uptake and color intensity. Experimentally, the color space components L^*, a^* and b^* values for the PET-E fabric and the PET-W fabric are listed in Table 1, where L^* is the brightness value, a^* is the red/green value, and b^* is the yellow/blue value. A lower L^* value corresponds to the PET-E fabric, indicating a darker color. In comparison, a higher L^* value corresponds to the PET-W fabric, indicating a brighter color. In addition, the PET-W fabric has positive a^* value, consistent with its reddish-orange color. The polarity of the solvent influences color shade through the solvent system.

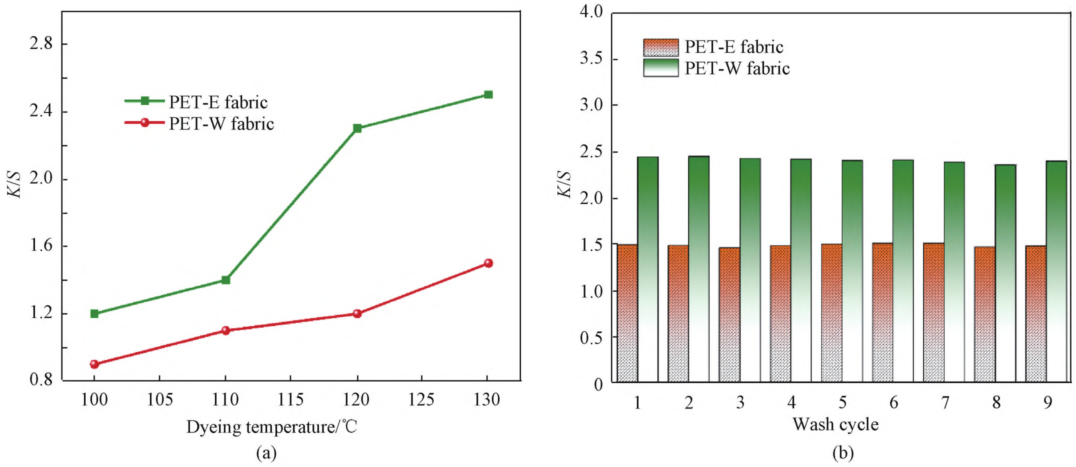


Fig. 7 *K/S* value with different factors: (a) dyeing temperature; (b) wash cycle

Table 1 Colorimetric assessment for dyed PET fabric

Sample	*K/S*	L^*	a^*	b^*
PET-E fabric	2.44	8.41	−0.91	−2.50
PET-W fabric	1.50	9.68	0.16	−1.16

2.6 Hydrophilic properties

PET fabric is a synthetic polymer that is moisture-resistant. The hydrophobic nature of the PET fabric is primarily attributed to its chemical structure, which lacks hydrophilic functional groups that readily interact with water molecules. However, both surface roughness and intermolecular forces play a role in determining the wettability of the PET fabric surface. Figure 8(a) shows that the PET fabric has a WCA of 120°, which means that the PET fabric is hydrophobic. After dyeing with lawsone dye, the WCA decreases, and the sample becomes hydrophilic. Lawsone on the PET fabric improves the wettability. The intermolecular forces, such as van der Waals force and hydrogen bonding, could affect the interaction between the liquid and the PET fabric surface. It is observed that a water droplet on the surface of the undyed PET fabric maintains its shape without spreading, whereas a water droplet on the surface of the dyed PET fabric spreads and is absorbed within several seconds (Fig. 8(b)).

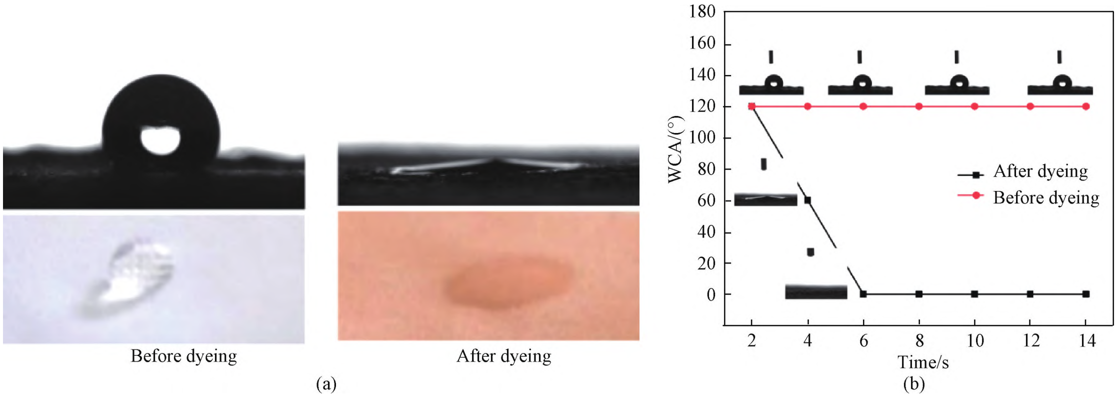


Fig. 8 Wettability of PET fabric before and after dyeing: (a) water droplet images; (b) WCA

2.7 Antistatic properties

The fabric's moisture absorption and retention characteristics are crucial for its antistatic properties[20]. As seen in Fig. 9, the moisture regain of the PET fabric is 0.6, which is attributed to its hydrophobic properties. However, after dyeing with LDS, there is an increase in moisture regain for both PET-W and PET-E fabrics.

Figure 10 shows the electrostatic induction characteristics related to the changes in relative humidity. The PET fabric generates a static voltage between 600 V and 800 V when the relative humidity is between 37% and 52%. However, the PET-E fabric and the PET-W fabric produce static voltage above 700 V in the lower relative humidity range (37% – 40%). In the higher relative humidity range (43% – 52%), the static voltages generated by the PET-E fabric and the PET-W fabric are lower than 700 V, and decrease to 370 V and 300 V at a relative humidity of 52%, respectively. This is because the surface hygroscopicity of the PET fabric is enhanced after dyeing, which increases the conductivity of the PET fabric surface, thereby providing an antistatic effect.

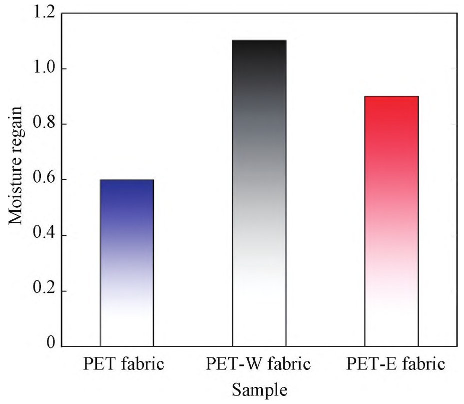


Fig. 9 Moisture regain of PET fabric before and after dyeing

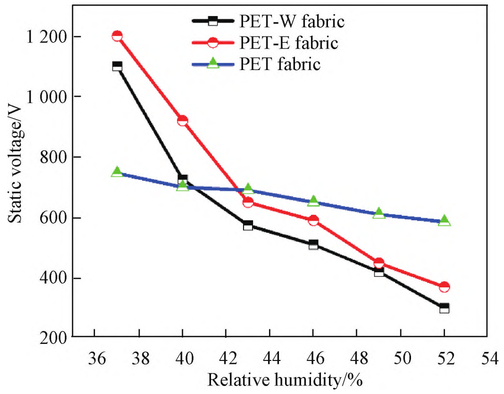


Fig. 10 Static voltage of PET fabric before and after dyeing

3 Conclusions

This work investigates the influence of lawsone dye in different solvent systems on the surface properties of the PET fabric. The PET fabric achieves hydrophilicity after dyeing, as indicated by the decrease in the WCA. Nevertheless, the enhanced moisture regain leads to a decrease in static voltage. At a relative humidity of 52%, the static voltages generated by the PET-E fabric and the PET-W fabric are only 370 V and 300 V, respectively. Both ethanol and deionized water influence the dyeing of the PET fabric, resulting in a durable color. The PET-E fabric exhibits a higher K/S value, indicating better color depth and dye absorption efficiency. Meanwhile, the PET-W fabric has higher positive values of L^* and a^*, indicating a brighter and more reddish color.

This approach successfully integrates environmentally friendly materials and cost-effective techniques, making it applicable not only to comfortable clothing but also to a wide range of other applications. Despite these advantages, optimizing dyeing processes to achieve optimal material properties remains a challenge. Future research could focus on refining these processes to enhance performance and sustainability.

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指甲花醌染料对 PET 织物表面特性的影响

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摘　要：为了提高聚对苯二甲酸乙二醇酯（polyethylene terephthalate，PET）织物的亲水性和抗静电性能，使用指甲花醌染料对 PET 织物进行染色。指甲花醌染料分别溶于乙醇/去离子水溶液和去离子水，制得不同指甲花醌染料溶液。探讨了指甲花醌染料如何改善 PET 织物的表面性能和颜色耐久性。使用红外染色机加速指甲花醌与 PET 织物之间的反应。采用傅里叶变换红外光谱、X 射线光电子能谱、X 射线衍射和紫外−可见分光光度法等技术验证了染色 PET 织物的化学组成。通过测定 K/S 值评估颜色耐久性。染色后，PET 织物表现出高亲水性。这提高了 PET 织物的吸湿性，增加了 PET 织物表面的导电性，使 PET 织物表现出抗静电效果。

关键词：聚对苯二甲酸乙二醇酯（PET）；指甲花醌；亲水性；抗静电