High-performance Hydrochromic Cotton Fabric Fabricated With CoCl2/waterborne Polyurethane for Air Humidity Detection

Jinju Zhang  
Jiangnan University

Fangqing Ge  
Jiangnan University

Jialing Tan  
Jiangnan University

Yunjie Yin  
Jiangnan University

Chaoxia Wang (✉ wangchaoxia@sohu.com)  
Jiangnan University  https://orcid.org/0000-0001-6322-7606

Research Article

Keywords: waterborne polyurethane, CoCl2, hydrochromic, cotton fabric, humidity detection

Posted Date: September 21st, 2021

DOI: https://doi.org/10.21203/rs.3.rs-889278/v1

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Abstract

Hydrochromic materials has been a novel topic in the research of stimuli-responsive sensors and anticounterfeiting encryption. A high-performance hydrochromic cotton fabric is fabricated with CoCl$_2$/waterborne polyurethane via hot-press method. Moisture sensing metal salt cobalt chloride is introduced into waterborne polyurethane via physical doping to induce hydrochromic phenomenon. The hydrochromic cotton fabric possess superior fastness due to the hydrogen bonds formed by hydroxyl group on cotton fabric and carbonyl group, urethane bond, ether bond in waterborne polyurethane. Meanwhile, the hydroxyl group on cotton fabric and waterborne polyurethane endow hydrochromic cotton fabric with excellent hydrophilicity and high humidity sensitivity. Air humidity could be easily detected by hydrochromic cotton fabric. The absorption of humidity in rainy days led to pink color, resulting in a blue shift at 512 nm. In contrast, hydrochromic cotton fabric turn to blue color below RH 59% in sunny days, leading to a red shift for up to 674 nm. Moreover, the hydrochromic cotton fabric exhibited eminent stability and cyclicity in response to either dry state or wet condition. Based on these excellent properties, hydrochromic cotton fabric fabricated with CoCl$_2$/waterborne polyurethane are promising as smart sensors with potential application in sensitive RH detector, anti-counterfeiting technology and decorative coatings.

1. Introduction

Stimuli-responsive chromic materials(Yang et al. 2018; Jia et al. 2021; Liu et al. 2021; Samanta et al. 2021) such as photochromic,(Qi et al. 2021; Yang et al. 2021) hydrochromic,(Si et al. 2021; Sun et al. 2021) thermochromic,(Zhang et al. 2020; Kim et al. 2021) and electrochromic(Kim et al. 2010; Nguyen et al. 2021) that exhibit a colorimetric response to external stimuli are extensively investigated due to their novelty in popular culture and potential applications.(Eoh et al. 2021; Ma et al. 2021; Si et al. 2021) Of the stimuli-responsive chromic materials, the hydrochromic materials,(Mishra and Singh 2021) which undergo colorimetric transitions upon interaction with humidity or water, have been widely used for monitoring atmospheric humidity(Park et al. 2016a; Bilgin and Backhaus 2020) and shows important applications in sensors,(Sheng et al. 2014; Park et al. 2016a, b; Bilgin and Backhaus 2020) environmental monitoring,(Zhou et al. 2021) displays(Sheng et al. 2014; Ju et al. 2020) and anticounterfeiting encryption(Ju et al. 2020; Yu et al. 2020).

Hydrochromic materials which can change their color once a stimulus is applied can both detect a change in conditions and convey it to a user.(You et al. 2017; Hong et al. 2018) Compared with thermochromic, electrochromic, and photochromic strategies, hydrochromic materials are easy to authenticate by the naked eye without external instruments. Hydrochromic materials have a broad spectrum of applications,(Park et al. 2016b; Ni et al. 2019) such as breath detection, air humidity detection,(Zhou et al. 2021) anticounterfeiting encryption inks,(Kou et al. 2018) water content sensors,(Karimipour et al. 2020; Sun et al. 2021) rewritable papers(Mao et al. 2021), and human sweat pore mapping technologies.(Kitamura et al. 2018) Hydrochromic materials include graphene oxide,(Chi et al. 2021) triarylmethane proton transfer,(Jiang et al. 2021) metal salt with crystal water, photonic crystals
(PCs), (Jung et al. 2021) polydiacetylenes (PDAs), cholesteric liquid crystals, (Stumpel et al. 2015; Meng et al. 2020; Momtaz and Chen 2020; Yoo et al. 2020) lanthanide-ion-coordinated supramolecular hydrogel (Yao et al. 2020), aggregation-induced-emission (AIE) molecular, (Jiang et al. 2021) and covalent organic framework (Kitamura et al. 2018).

Recently, many researchers have made considerable efforts to design and exploit new methods to develop hydrochromic materials and extend their applications. For example, Yang's (Lan et al. 2021) group prepared a bilayer film consisting of composed of liquid crystalline networks (LCN) film and hydrochromic aggregation-induced emission molecule-doped hydrophilic layer. The composite film can deform and change color when exposed to different humidity. Zhou's (Shi et al. 2021) group prepared a semi-interpenetrating network composed of a cholesteric main-chain polymer and a hygroscopic poly(ampholyte) to obtain obtained a dual responsive elastic cholesteric polymer material. When swelled with water, the material showed a redshift of the reflected color. Gao's (Bu et al. 2021) group synthesized vinylene-linked covalent organic frameworks VCOF-PyrBpy, showing fluorescent response to water due to hydrogen bonding and protonation. Wang's (Mao et al. 2021) group demonstrated an efficient and convenient strategy to fabricate rewritable paper based on reversible hydrochromism of donor-acceptor Stenhouse adducts (DASAs).

However, the complexity of the preparation process and discoloration mechanism limit its practical applications. Typical colorimetric RH indicator such as CoCl$_2$-based humidity sensor have been presented due to its advantages of high sensitivity and reliability. (Xu et al. 2021) Long’s group (You et al. 2017) fabricated humidity indicators based on composite polyamide 66/cobalt chloride (PA66/CoCl$_2$) nanofibrous membranes by electrospinning, which showed obviously color change from blue to pink as relative humidity (RH) increasing from 12.4 to 97.2%. Mariana-Dana Damaceanu (Damaceanu et al. 2016) prepared CoCl$_2$/polyimide hybrid materials, which showed a visible color change when exposed to moisture and reverted immediately to the original color by heating to reduce the humidity.

Moisture sensing metal salt cobalt chloride could be introduced into waterborne polyurethane via physical doping to induce hydrochromic phenomenon. Waterborne polyurethane is suitable for hydrochromic materials in the textile field because of its safe non-toxic properties and green environmentally friendly performances. (Wen et al. 2019; Zhang et al. 2019) Moreover, the hydrophilicity of waterborne polyurethane promotes the moisture absorption process of hydrochromic materials. (Dai et al. 2021)

In this work, we have successfully synthesized CoCl$_2$·6H$_2$O/waterborne polyurethane hybrid films and connected with cotton fabric under the force of chemical cross-linking by hot-press method. The test methods of FTIR proved the successful preparation of CoCl$_2$·6H$_2$O/waterborne polyurethane hybrid films. The discoloration mechanism of CoCl$_2$·6H$_2$O was explored by UV-vis test. The molecular weight, thermal performance and wetting performance of CoCl$_2$·6H$_2$O/waterborne polyurethane hybrid films were investigated. The discoloration performance and discoloration fatigue resistance of hydrochromic cotton fabrics were systematically characterized. The results showed that hydrochromic cotton fabric exhibiting
high humidity sensitivity with obviously color change, superior fastness, outstanding reversibility and admirable thermal stability, implying this hydrochromic material a potential candidate in application of stimuli-responsive sensors, efficient RH detector, anti-counterfeiting technology and decorative coatings.

2. Experimental Section

2.1 Materials

Isophorone diisocyanate (IPDI) and Polycarbonate diol (PCDL2000) were acquired from Shanghai Aladdin Reagent Co., Ltd. Butyl tin dilaurate (DBTDL) and 2,2-Dihydroxymethyl butyric acid (DMBA) were obtained from Shanghai Macklin Biochemical Technology Co., Ltd. Butanediol (BDO) and triethylamine (TEA) were purchased from Sinopharm Chemical Reagent Co., Ltd. Tetrahydrofuran (THF), acetone, ethanol and N,N-Dimethylformamide (DMF) were supplied by Sinopharm Chemical Reagent Co., Ltd. Lithium chloride (LiCl), Sodium Bromide (NaBr), Sodium chloride (NaCl), Potassium chloride (KCl) and Potassium sulfate (K₂SO₄) were also obtained from Sinopharm Chemical Reagent Co., Ltd. Cotton fabric (150 g/m²) was purchased from a local factory.

2.2 Synthesis of CoCl₂·6H₂O/waterborne polyurethane hybrid materials

Dissolve 6.68 g isophorone diisocyanate (IPDI) and 20 g polycarbonate diol 2000 (PCDL2000) in 10 ml tetrahydrofuran (THF) into a three-necked flask, and add 0.2 mL butyl tin dilaurate (DBTDL). The reaction was conducted at 80 °C with 300 r/min mechanical stirring for 1.5 h. Then, 0.74 g 2,2-Dimethylolbutyric acid (DMBA) was dissolved in 10 mL THF and added slowly to the pre-polymerized product. The oil bath reacted for 2 h with 400 r/min mechanical stirring. 0.90 g 1,4-butanediol (BDO) was added slowly to the system at 80 °C for an additional 2 h. 0.51 g triethylamine (TEA) was added for neutralize the reaction at 40 °C for 0.5 h. Finally, 3 g/2 g/1 g/0 g CoCl₂·6H₂O was dissolved in 10 mL THF respectively, and added to the three-necked flask at a speed of 300 r/min under mechanical stirring for 20 min. The prepared CoCl₂·6H₂O/waterborne polyurethane hybrid materials were dried in a polytetrafluoroethylene mold. The schematic diagram of the synthesis of CoCl₂·6H₂O/waterborne polyurethane hybrid materials is shown in Scheme 1.

2.3 Preparation of CoCl₂·6H₂O/waterborne polyurethane (CoPU) films

The dried CoCl₂·6H₂O/waterborne polyurethane hybrid materials were weighed 15 g respectively and dissolved in 73 ml of dichloromethane solvent, and dried at room temperature to obtain a uniform CoCl₂·6H₂O/waterborne polyurethane (CoPU) films. The waterborne polyurethane doped with 0 g CoCl₂·6H₂O was named as PU. The waterborne polyurethane doped with 1 g CoCl₂·6H₂O was named as Co₁PU. The waterborne polyurethane doped with 2 g CoCl₂·6H₂O was named as Co₂PU. The waterborne
polyurethane doped with 3g CoCl$_2$·6H$_2$O was named as Co$_3$PU. The molar ratio of each component is illustrated in Table 1.

Table 1. The proportion of components of CoCl$_2$·6H$_2$O/waterborne polyurethane (CoPU) films.

| Samples | Weight/g | IPDI | PCDL2000 | DMBA | BDO | CoCl$_2$·6H$_2$O |
|---------|----------|------|----------|------|-----|-----------------|
| PU      | 6.68     | 20.00| 0.74     | 0.90 | 0   |                 |
| Co$_1$PU| 6.68     | 20.00| 0.74     | 0.90 | 1   |                 |
| Co$_2$PU| 6.68     | 20.00| 0.74     | 0.90 | 2   |                 |
| Co$_3$PU| 6.68     | 20.00| 0.74     | 0.90 | 3   |                 |

2.4 Preparation of CoPU hydrochromic cotton fabric

15g of CoCl$_2$·6H$_2$O/waterborne polyurethane (CoPU) films were weighed for hot-press on 15*15cm cotton fabric. The hot-press process was conducted at 50 °C with 10MPa pressure for 10 min and 20MPa pressure for an additional 15min. Finally, CoPU hydrochromic cotton fabrics with 0.5mm thick were obtained. The samples were named as PU hydrochromic cotton fabric, Co$_1$PU hydrochromic cotton fabric, Co$_2$PU hydrochromic cotton fabric, Co$_3$PU hydrochromic cotton fabric respectively.

2.5 Characterization and Measurements

UV–vis spectra of CoCl$_2$·6H$_2$O in H$_2$O, acetone, ethanol and N, N-Dimethylformamide (DMF) were acquired by using a UV-vis Spectrophotometer (Cary 50, Varian) under room temperature.

The Fourier transform infrared (FT-IR) spectra of PU, Co$_1$PU, Co$_2$PU, Co$_3$PU were monitored with a NICOLET is10 transform infrared instrument (Thermo Fisher Scientific, Co. Ltd., China). Measurements were carried out within the wavenumber range of 500–4000 cm$^{-1}$ under room temperature. The vitrification temperatures of PU, Co$_1$PU, Co$_2$PU and Co$_3$PU were tested by differential thermal scanning calorimeter (Q200). Before the test, the polyurethane samples were placed in an oven at 80 °C for 24 h to remove the solvent, and about 5 mg of the samples were weighed and put into a crucible for testing. The testing temperature range was -80 °C to 200 °C. The heating rate was 10 °C/min, and the flow rate of nitrogen was 50 mL/min. A thermogravimetric analyzer (Q500) was used to study the thermal properties of PU, Co$_1$PU, Co$_2$PU, and Co$_3$PU. 4-6 mg of dried polyurethane were weighed into a crucible for thermal performance analysis. The test temperature range was set to 25~500 °C, and the heating rate was 20 °C/min. The measurement was performed under a nitrogen atmosphere. Gel permeation chromatography (GPC, Waters THF, USA) was applied to analyze the molecular weight distributions of polyurethanes at 35
°C with THF as the mobile phase. Approximately 20 μL of a polyurethane solution with a concentration of 10 mg/mL was injected.

The surface morphologies of PU, Co₁,PU, Co₂,PU, Co₃,PU hydrochromic cotton fabric were observed by scanning electron microscopy (SEM, Carl Zeiss Microscopy, Germany) under room temperature. The chemical compositions of Co₃,PU hydrochromic cotton fabric was characterized by energy dispersive spectroscopy (EDS). The structures of CoCl₂·6H₂O and Co₁,PU, Co₂,PU, Co₃,PU hydrochromic cotton fabric were characterized by X-ray diffractometer from Japan over the 2θ range of 5–80°. The contact angle (CA) of PU, Co₁,PU, Co₂,PU, Co₃,PU hydrochromic cotton fabric measurements were carried out by a Drop Shape Analyzer 100 (Krüss, German) using liquid droplets of 5 μL in volume.

The color parameters (a*, b*, L*, K/S value) of Co₁,PU, Co₂,PU, Co₃,PU hydrochromic cotton fabric were tested by an Xrite-8400 spectrophotometer under a D65 illuminant using a 10° standard observer. The K/S value represents the apparent color depth. Water vapor capture was measured by setting dried Co₁,PU, Co₂,PU, Co₃,PU hydrochromic cotton fabric in a humidity container with controllable RH on the basis of the saturated salt solution composition. The various saturated salt solutions with different humidity gradients (RH 11%, RH 59%, RH 75%, RH 85%, RH98%) were prepared with saturated anhydrous LiBr, LiCl, CH₃COOK, NaBr, KCl solutions and distilled water. Heating to 60°C represent RH 0%, breathing or using a humidifier to reach RH 100%. These glass containers were placed at 25°C. After equilibration, Co₁,PU, Co₂,PU, Co₃,PU hydrochromic cotton fabrics were placed in the above different humidity gradients microenvironment. Then, the color parameters of Co₁,PU, Co₂,PU, Co₃,PU hydrochromic cotton fabrics were obtained by Xrite-8400 spectrophotometer under a D65 illuminant. The washing fastness and rubbing fastness of CoPU hydrochromic cotton fabrics were determined in accordance with AATCC 61-2006 and AATCC 8-2007 standards respectively. The color fastness of CoPU hydrochromic cotton fabrics were evaluated by gray sample card.

3. Results And Discussion

3.1 Hydrochromic behavior of CoCl₂·6H₂O

Hydrochromic performance of CoCl₂·6H₂O in H₂O, acetone, ethanol and N, N-Dimethylformamide (DMF) were investigated, respectively. As shown in Fig.1, the CoCl₂·6H₂O/H₂O solution displayed pink color, and the corresponding absorption peak was at 512 nm. CoCl₂·6H₂O combines with water molecules to form [Co·(H₂O)₆]²⁺, so that the salt solution [Co·(H₂O)₆]²⁺·2Cl⁻ exhibits pink color. While CoCl₂·6H₂O in acetone, ethanol and N, N-Dimethylformamide (DMF) solution displayed blue color. The blue color is the darkest in DMF with two absorption bands centered at 674 nm and 608 nm, followed by acetone with two absorption bands centered at 674 nm and 580 nm, and the lightest blue in ethanol with an absorption band centered at 658 nm. The polarity of the three organic solvents is, N, N-Dimethylformamide (DMF), acetone and ethanol, so CoCl₂·6H₂O in acetone, ethanol and N, N-Dimethylformamide (DMF) solution displayed different shades of blue color. When CoCl₂·6H₂O was in an organic solvent, its two crystal
waters were taken by the solvent with high polarity, and the CoCl$_2$·6H$_2$O that loses two crystal waters changed from red to blue.

### 3.2 Synthesis and structural characterization of CoPU films

To demonstrate the successful synthesis of polyurethane, the chemical structures of CoCl$_2$·6H$_2$O/waterborne polyurethane (CoPU) films were tested (Fig. 2). The disappearance of the absorption peak at 2270 cm$^{-1}$ and the appearance of N-H in the carbamate at 3387 cm$^{-1}$ and C=O at 1739 cm$^{-1}$ proved the successful synthesis of PU. The typical absorption peak at 1739 cm$^{-1}$ was ascribed to C=O stretching vibration, and the peak at 1242 cm$^{-1}$ was assigned to C-O-C stretching vibration, indicating that polycarbonate diol 2000 (PCDL2000) was successfully introduced into the polyurethane polymer chain. The successful access of PCDL2000 can improve the hydrophilicity of polyurethane, which is beneficial to the humidity-sensitive discoloration ability of CoCl$_2$·6H$_2$O/waterborne polyurethane (CoPU) films.

### 3.3 Molecular weight and thermal stability of CoPU films

We summarized the number average weight (Mn), the weight average molecular weight (Mw), the molecular weight at the midpoint (retention time) of the normal distribution of molecular weight (Mp) and polydispersity indexes (PDI) of the prepared polyurethane in Fig.3. The results showed that the number average molecular weights (Mn) of the prepared polyurethane was 12180. Therefore, the prepared polyurethane has moderate hardness, which is suitable for hot pressing on cotton fabric. Appropriate hardness of the prepared polyurethane also plays a significant role in hydrochromic process. High molecular weight causes polyurethane to be too hard, retarding its hygroscopicity process. Low molecular weight causes polyurethane to be too soft, making the surface become sticky after hygroscopic process. The results were found that PDI of the prepared polyurethane was 1.71. The prepared polyurethane exhibited small PDI, which possessed good uniformity.

In order to investigate the thermal performance of CoCl$_2$·6H$_2$O, PU, Co$_1$PU, Co$_2$PU, Co$_3$PU, the thermosgravimetric curves of TGA and DTG were demonstrated in Fig.4. Thermal degradation process of CoCl$_2$·6H$_2$O, PU, Co$_1$PU, Co$_2$PU, Co$_3$PU were recorded in Fig.4. In Fig.4(b), thermal degradation process of CoCl$_2$·6H$_2$O can be split into two stages. Firstly, degradation of crystal waters occurred around 100 °C. The weight of CoCl$_2$·6H$_2$O lost 15.42%, which indicating that CoCl$_2$·6H$_2$O lost two crystal waters. In the second stage, the maximum degradation rates were corresponding to 780.8 °C. The weight of CoCl$_2$·6H$_2$O lost completely, which indicating that CoCl$_2$·6H$_2$O lost six crystal waters and the entire system was almost completely degraded due to the high temperature at this stage. Therefore, the hydrochromic mechanism of cobalt chloride is the loss of two crystal waters at low temperature. In Fig.4(c), thermal degradation process of the prepared polyurethane can be divided into two stages. In the first stage, the degradation temperature was below 200 °C, which was attributed to moisture and residual solvent. The second decomposition range was occurred at 300-400 °C due to the dissociation of urethane bonds to
break the macromolecular chain. In Fig.4(d-f), thermal degradation process of CoCl$_2$·6H$_2$O/waterborne polyurethane (CoPU) films can be divided into two stages. The degradation temperature in the first stage was below 200 °C attributed to moisture and residual solvent. The second stage above 300 °C is the degradation process of urethane bonds dissociation, which is the process of maximum weightlessness. The maximum weightlessness temperature was 335.47 °C, 330.0 °C and 330.8 °C, respectively. This proves that CoPU films have good thermal stability. High temperature accelerates water vapor evaporation, so high thermal degradation temperature of CoPU films will not affect the hydrochromic performance of CoPU films.

The thermal performance of CoCl$_2$·6H$_2$O/waterborne polyurethane (CoPU) films with different CoCl$_2$·6H$_2$O contents was obtained by DSC curves as plotted in Fig.5. It was found that the glass transition temperature (Tg) of the prepared polyurethane was around −17.6°C, demonstrating that the prepared polyurethane exhibited high fluidity at room temperature. According to the DSC curves of CoPU films in Fig. 5, it can be concluded that the glass transition temperatures of Co$_1$PU, Co$_2$PU and Co$_3$PU were −24.5 °C, −37.6 °C and −17.8 °C, respectively. The low glass transition temperature (Tg) of CoCl$_2$·6H$_2$O/waterborne polyurethane (CoPU) films made it highly elastic at room temperature. The segments of CoPU films started to move at room temperature, accelerating moisture absorption process. As a result, low glass transition temperature (Tg) improves the sensitivity of hydrochromic process.

3.4 Characterizations of CoPU hydrochromic cotton fabric

In order to further improve the moisture absorption sensitivity of CoCl$_2$·6H$_2$O/waterborne polyurethane (CoPU) films, the CoPU films were combined with cotton fabric by hot pressing. The surface morphologies of cotton fabric and CoPU hydrochromic cotton fabrics were examined by SEM (Fig. 6). It is obvious that the surface of cotton fabrics were clearly distributed fibers, while the surface of CoPU hydrochromic cotton fabrics were coated with smooth films, proving CoCl$_2$·6H$_2$O/waterborne polyurethane (CoPU) films has been combined onto the surface of cotton fabrics firmly. The hydroxyl group on the cotton fabric and the carbonyl group, urethane bond and ether bond in the CoPU films form hydrogen bonds, so that the CoPU hydrochromic cotton fabric has good fastness. Meanwhile, the hydroxyl group on the cotton fabric and the hydroxyl group in the CoPU films possessed CoPU hydrochromic cotton fabric good hydrophilicity, making it easier to capture water molecules in the environment. Moreover, the close contact between CoPU films and cotton fabric made CoPU hydrochromic cotton fabric capture water molecules in the air, so that CoPU hydrochromic cotton fabric showed rapid response to humidity change.

The chemical compositions of Co$_3$PU hydrochromic cotton fabric surface were examined through the EDS analysis. As shown in Fig.7, elemental mappings of Co$_3$PU hydrochromic cotton fabric showed that the distribution of Co and Cl were uniform across the whole Co$_3$PU hydrochromic cotton fabric surface, demonstrating that CoCl$_2$·6H$_2$O has been successfully introduced into the prepared waterborne polyurethane and Co$_3$PU films were well combined onto the surface of cotton fabric.
The crystalline structures of CoCl$_2$·6H$_2$O and CoPU hydrochromic cotton fabric were identified by X-ray diffraction (XRD). The XRD patterns of CoCl$_2$·6H$_2$O was described in Fig.8. CoCl$_2$·6H$_2$O had corresponding crystalline structure at 2θ=16.55°, 21.13°, 33.54°, 38.28°, and 44.12° characteristic diffraction peaks. After hot-press process, the characteristic diffraction peaks of CoCl$_2$·6H$_2$O crystalline structure were reflected on CoPU hydrochromic cotton fabric, which proved that CoPU films were combined with the surface of cotton fabric firmly.

Considering that CoPU hydrochromic cotton fabric will be subjected to wet conditions during hydrochromic process, the contact angle of CoPU hydrochromic cotton fabric should be tested. The contact angle of Co$_0$PU hydrochromic cotton fabric, Co$_1$PU hydrochromic cotton fabric, Co$_2$PU hydrochromic cotton fabric, and Co$_3$PU hydrochromic cotton fabric were tested. The results were shown in Fig. 9. The water contact angle of Co$_0$PU, Co$_1$PU, Co$_2$PU, and Co$_3$PU were 63.32°, 64.10°, 63.87°, and 66.62°, respectively. The data showed that CoPU hydrochromic cotton fabric had strong hydrophilicity. Furthermore, strong hydrophilicity provided a prerequisite for the hydrochromic performance of CoPU hydrochromic cotton fabric.

### 3.5 Humidity-sensitive discoloration performance and mechanism of CoPU hydrochromic cotton fabric

The amount of moisture in the environment is of vital importance in affecting the discoloration of CoPU hydrochromic cotton fabric. In order to analyze the hydrochromic performance of CoPU hydrochromic cotton fabric, color parameters were monitored by a computer color measurement and color matching instrument. The results are shown in Fig. 10. After being placed in increasing humidity container, the a* value of Co$_1$PU hydrochromic cotton fabric changed from -11.99 to 12.39, the b* value of Co$_1$PU hydrochromic cotton fabric changed from -17.19 to -2.54, and the corresponding discoloration was changed from blue to pink. While the a* value of Co$_2$PU hydrochromic cotton fabric changed from -21.85 to 12.88, the b* value of Co$_2$PU hydrochromic cotton fabric changed from -23.72 to -1.95, and the corresponding discoloration was changed from blue to pink. At the same time, the a* value of Co$_3$PU hydrochromic cotton fabric changed from -6.61 to 14.05, the b* value of Co$_3$PU hydrochromic cotton fabric changed from -38.96 to 0.16, and the corresponding discoloration was changed from blue to pink.

As shown in Fig 10, CoPU hydrochromic cotton fabrics exhibited blue color below RH59%, and turned to pink color above RH59%. With the change of hue, the peaks of the corresponding K/S value also changed. Notably, as the amount of CoCl$_2$·6H$_2$O increased, the color below RH59% became bluer and the color above RH59% became pinker. The increase of CoCl$_2$·6H$_2$O would increase the degree of CoCl$_2$·6H$_2$O content in CoPU films, which can increase the depth of color to some degree. More interestingly, compared with other hydrochromic materials, the color change of CoPU hydrochromic cotton fabric was a process of color mutation at RH 59%.

Due to their excellent hydrochromic performance, CoPU hydrochromic cotton fabrics were applied to fabricate barometer. In sunny days, there exists low humidity in the atmosphere, the moisture on the
CoPU hydrochromic fabrics become less, and CoCl$_2$·6H$_2$O in the CoPU films lose two crystal waters and show blue color. When it is rainy, environment humidity is high, the CoPU hydrochromic fabrics absorb moisture. CoPU films regain crystal water and turn to pink color. That is blue color in sunny days while pink color in rainy days. Moreover, the hydroxyl group on the cotton fabric and the prepared polyurethane possessed CoPU hydrochromic cotton fabrics good hydrophilicity and superior humidity sensitivity. Furthermore, the hydrogen bonds formed between hydroxyl group on cotton fabric and carbonyl group, urethane bond, ether bond in the CoPU films made CoPU hydrochromic cotton fabric obtained good fastness. Totally, the observations reveal that CoPU hydrochromic cotton fabric could be employed in monitoring weather changes through color change.

In order to characterize the humidity-sensitive discoloration reversibility of CoPU hydrochromic cotton fabric, a more concrete study on the color-change of CoPU hydrochromic cotton fabric was conducted by analyzing the variation of $a^*$ and $b^*$ values during drying and wetting. The results were showed in Fig12, it can be seen that in the 10 measured cycles, $a^*$ and $b^*$ values of CoPU hydrochromic cotton fabric had no obvious change. The K/S value of CoPU hydrochromic cotton fabric was at 670 nm, and the color appeared blue. In 10 cycles, the $a^*$ value of Co$_1$PU hydrochromic cotton fabric was about -20 in dry conditions and 8 in wet conditions, while $b^*$ value of Co$_1$PU hydrochromic cotton fabric was about -15 in dry conditions and 5 in wet conditions. The $a^*$ value of Co$_2$PU hydrochromic cotton fabric was about -25 in dry conditions and 8 in wet conditions, while $b^*$ value of Co$_2$PU hydrochromic cotton fabric was about -20 in dry conditions and 5 in wet conditions. The $a^*$ value of Co$_3$PU hydrochromic cotton fabric was about -25 in dry conditions and 10 in wet conditions, while $b^*$ value of Co$_3$PU hydrochromic cotton fabric was about -25 in dry conditions and 7 in wet conditions. It can be concluded that with the increasement of CoCl$_2$·6H$_2$O, the CoPU hydrochromic cotton fabric exhibited deeper bluer color in dry conditions while slightly pink color change in wet conditions. In 10 cycles, CoPU hydrochromic cotton fabric alternately reciprocated between blue and pink. In summary, CoPU hydrochromic cotton fabric owns the superior stability and repeatability.

The durability of CoPU hydrochromic cotton fabrics were tested (Table 2). The wet rubbing fastness and washing fastness were investigated, respectively. For wet rub fastness, the discoloring fastness and staining fastness of CoPU hydrochromic cotton fabrics have reached 3−4 grade and 4 grade. Meanwhile, for washing fastness, the discoloring fastness and staining fastness of CoPU hydrochromic cotton fabrics have reached 3 grade and 3−4 grade. CoCl$_2$·6H$_2$O was wrapped in the prepared polyurethane, making it difficult for water and external forces to remove CoCl$_2$·6H$_2$O from the prepared polyurethane. Simultaneously, the good color fastness of CoPU hydrochromic cotton fabrics can be contributed to the formation of hydrogen bonds between hydroxyl group on cotton fabrics and the carbonyl group, urethane bond, ether bond in the CoPU films.

**Table 2** Color fastness of CoPU hydrochromic cotton fabrics.
### Samples

| Samples | Wet rub fastness(grade) | Washing fastness(grade) |
|---------|-------------------------|-------------------------|
|         | Discoloring | Staining | Discoloring | Staining |
| Co\(_1\)PU | 3-4 | 4 | 3 | 3-4 |
| Co\(_2\)PU | 3-4 | 4 | 3-4 | 3 |
| Co\(_3\)PU | 3-4 | 4 | 3 | 3 |

### 4. Conclusion

In this work, we have successfully developed hydrochromic cotton fabric based on CoCl\(_2\)/waterborne polyurethane by facial hot-pressing method. Hydrochromic performance was constructed by moisture sensing metal salt cobalt chloride doped into waterborne polyurethane. The hydrogen bonds formed between cotton fabric and waterborne polyurethane possessed hydrochromic cotton fabric superior fastness. Moreover, hydrochromic cotton fabric obtained excellent hydrophilicity and high humidity sensitivity due to the hydroxyl group on cotton fabric and waterborne polyurethane. Hydrochromic cotton fabric presented pink color with a blue shift for up to 512 nm above RH 59%, while turned to blue color with a red shift for up to 674 nm below RH 59%. More interestingly, upon exposure to sunny and rainy days, hydrochromic cotton fabric presented blue and pink color, respectively, realizing air humidity monitoring. In 10 wet-dry cycles, the color of hydrochromic cotton fabric had no obvious change, showing eminent reversibility. In summary, this kind of hydrochromic cotton fabric fabricated with CoCl\(_2\)/waterborne polyurethane possess high humidity sensitivity, superior fastness, outstanding reversibility and admirable thermal stability is promised to be used in a wide range of applications, such as stimuli-responsive sensors, efficient RH detector, anti-counterfeiting technology and decorative coatings.

### Declarations

### Declaration of interests

The authors declare no competing financial interest.

### Acknowledgment

This study was financially supported by the National Natural Science Foundation of China (21975107), Natural Science Foundation of Jiangsu Province (SBK2019020945) and Fundamental Research Funds for the Central Universities (JUSRP51724B).

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Scheme 1

Scheme 1 is available in the Supplementary Files section.

Figures
Figure 1

UV-vis spectra of CoCl$_2$·6H$_2$O in H$_2$O, DMF, acetone and ethanol
Figure 2

FTIR spectra of CoCl2·6H2O/waterborne polyurethane (CoPU) films
Figure 3

GPC spectra of polyurethane (PU).

| Sample | $M_n$  | $M_w$  | $M_p$  | PDI |
|--------|--------|--------|--------|-----|
| PU     | 12180  | 20862  | 19200  | 1.71|
Figure 4

TG and DTG of (a) TG spectrum of CoCl2·6H2O and four polyurethanes; (b) CoCl2·6H2O; (c) PU; (d) Co1PU; (e) Co2PU; (f) Co3PU

Figure 5

DSC curves of CoCl2·6H2O/waterborne polyurethane (CoPU) films.
Figure 6

SEM images of (a1-a2) cotton fabric; (b1-b2) Co1PU hydrochromic cotton fabric; (c1-c2) Co2PU hydrochromic cotton fabric; (d1-d2) Co3PU hydrochromic cotton fabric.

Figure 7

EDS of Co3PU hydrochromic cotton fabric
Figure 8

XRD of CoPU hydrochromic cotton fabric
Figure 9

Analysis of contact angle of CoPU hydrochromic cotton fabric
Figure 10

Hydrochromic performance of CoPU hydrochromic cotton fabric (a) Co1PU hydrochromic cotton fabric; (b) Co2PU hydrochromic cotton fabric; (c) Co3PU hydrochromic cotton fabric.
Figure 11

Schematic diagram of the cyclic discoloration process of CoPU hydrochromic cotton fabric
Figure 12

Hydrochromic cycle performance of CoPU hydrochromic cotton fabric (a) Co1PU hydrochromic cotton fabric; (b) Co2PU hydrochromic cotton fabric; (c) Co3PU hydrochromic cotton fabric.

Supplementary Files

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- scheme1.jpg