

Hydrophilization of poly (lactic acid) fibre and its combination with dyeing and UV protection finishing

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A polyester-polyether block copolymer (PPBC) has been used to fabricate the hydrophilic surface on poly (lactic acid) (PLA) fibre by a simple exhaust finishing. The quantity of PPBC adsorption on PLA fibre is found to increase with increasing PPBC dosage and application temperature. A high temperature application is capable of facilitating the intercalation of the hydrophobic polyester moiety of PPBC into the inner surface layer of PLA fibre, and accordingly improving the laundry resistance of hydrophilicity effect. The PPBC finished PLA fibre exhibits good water wettability. Additionally, the integrated dyeing, hydrophilization and UV protection finishing in one bath is successfully performed. The uptake of disperse dyes and UV absorber by PLA fibre is adversely affected by PPBC, but both of them show almost no impact on the hydrophilization of PLA fibre. The UV absorber in PLA fibre is able to enhance the light resistance of dyeings.

Keywords: Block copolymers, Dyeing, Hydrophilicity, Poly(lactic acid) fibre, Polyester, Polyether, UV protection

1 Introduction

Poly(lactic acid) (PLA) has received considerable attention in textile industry mainly due to its production from an annually renewable resource, easy degradability, and better dyeability at low temperature compared to the most extensively used poly(ethylene terephthalate) (PET) fibre¹⁻³. However, PLA has some inherent drawbacks such as lack of reactive side-chain groups, poor hydrophilicity, brittleness, poor thermal resistance, poor mechanical and barrier properties, easy degradation during application and storage, high UV light transmittance, and poor durability of application^{1, 2, 4-9}. These drawbacks of PLA have become main limitations towards its large-scale commercial application in textile industry, and hence some efforts are being made to improve the properties of PLA fibre.

The hydrophobic nature of PLA fibre causes its limited capacity to adsorb sweat and humidity, giving a stuffy feeling when it serves as a clothing material. To improve the hydrophilicity of PLA fibre, some modification methods, such as lipolytic enzyme hydrolysis¹⁰, low temperature oxygen plasma¹¹, pulsed plasma polymerization of primary amine-controlled heptylamine¹², coating of glycol-

dimethyloldihydroxyethyleneurea¹³, photografting of acrylic acid and maleic anhydride¹⁴, and coating of bioacceptable polymers⁵, have been developed. Despite the above investigations, little attention has been paid to the hydrophilization of PLA fibre using a simple chemical process at low cost which is more suitable for industrial application. To impart the hydrophilicity to PLA fibre, an agent is more preferable, which can interact physically and strongly with PLA molecules with no impact on the hand feeling of PLA fabric. Polyester-polyether block copolymer (PPBC) bearing hydrophilic polyether and hydrophobic polyester chain segments has been used to the hydrophilic and soil-release finishing of PET fibre¹⁵⁻¹⁸. The polyester segments of PPBC have a strong attraction for the PET surface, whereas the polyether segments are left outside the surface, forming an invisible hydrophilic film^{16, 17}. In view of the structural similarity between PLA and PET fibres, the application of PPBC in the functional modification of PLA is worthy to be studied.

PLA matrix without aromatic moiety has inherently low capability of UV light absorption, thereby permitting high transmittance of UV light⁷⁻⁹. If PLA textile materials are used to manufacture outdoor products and summer clothes, they cannot effectively protect human skin from the sun's harsh rays. Therefore, some measures must be taken to block the

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transmission of UV light through PLA textiles. An additional benefit of shielding UV radiation is its ability to improve the light stability of the dyed PLA textiles. It is well known that the palely dyed textiles exhibit poorer resistance or colour fastness to light as well as higher UV light transmittance than the dark dyeings in which the dyes have UV absorption ability and can provide good UV protection function. Because the palely dyed clothes are widely employed in summer, their UV protection finishing becomes more essential. In order to block UV transmission and to protect PLA products from UV damage, inorganic nanoparticles and organic UV absorbers have been applied^{8,9,19-21}. The benzotriazole type UV absorber was found to decrease the photofading of dyed PLA fabrics⁸. The triazine-based UV absorber was successfully used to improve the UV protection performance of PLA fabrics in our previous work⁹.

In the light of the defects of PLA textiles in hydrophilicity and UV protection as well as the more application of the palely dyed clothes in summer, an attempt has been made to modify PLA fibre with a hydrophilic agent having the structure of polyester-polyether block copolymer and a triazine-based UV absorber by exhaust application with the aim of imparting hydrophilic and UV protective functions to PLA fabrics, and decreasing the photofading of the palely dyed fabrics. The adsorption property of hydrophilic agent, the hydrophilicity of modified PLA fabric, and the durability of hydrophilicity have been emphatically discussed. The simultaneous disperse dyeing, hydrophilization and UV protection finishing in one bath are also evaluated.

2 Materials and Methods

2.1 Materials

A polyester-polyether block copolymer (PPBC) was kindly offered by Zhangjiagang Duplus Chemical Co. Ltd., China. Disperse dyes (C.I. Disperse Yellow 82, Orange 30, Red 54, Red 74, Red 153, Blue 148 and Blue 183) were commercially obtained. The water-insoluble UV absorber (UV-Fast P) was kindly provided by Huntsman International, and its main ingredient is a derivative of 2,4,6-triphenyl-1,3,5-triazine. A standard synthetic detergent was bought from Shanghai White Cat Technology Co. Ltd., China. The knitted PLA fabric was purchased from Shandong Jide Ecological Technology Co. Ltd., China. To remove the spin oils added to PLA fibre, the fabric sample was scoured in the solution

containing 1 g/L sodium bicarbonate and 0.5 g/L nonionic surfactant (polyoxyethylene alkyl ether) at 60 °C for 30 min. The scoured fabric was then rinsed thoroughly in distilled water, and allowed to dry in the open air.

2.2 Functional Finishing and Dyeing

All the functional finishing and dyeing were carried out in the sealed and stainless steel dye pots housed in the FAD-7-18P infrared dyeing machine (Wuxi Yabo Textile Equipment Co., Ltd., China). The liquor ratio was kept at 40:1.

2.2.1 Hydrophilic Finishing

To assess the effect of PPBC dosage, the fabrics were treated with 0.5–2.5% (owf) PPBC solution. The fabrics were immersed into the PPBC solutions at 30 °C, and subsequently the solutions were heated to 100 °C at a heating rate of 2 °C/min. The treatment was continued for 50 min. The effect of application temperature was discussed by using 1.5% (owf) PPBC at 70, 80, 90, 100 and 110 °C for 80, 70, 60, 50 and 40 min respectively. At the end of each hydrophilic finishing, the PPBC solutions were cooled to 70 °C at a rate of 2 °C/min. Then the fabrics were removed, rinsed in distilled water, and finally allowed to dry in the open air.

2.2.2 Simultaneous Dyeing and Finishing

The simultaneous dyeing and finishing was carried out by combined application of disperse dyes together with a hydrophilic agent and/or a UV absorber. The solution was composed of 0.1% (owf) dyes, 2% (owf) PPBC and 0-10% (owf) UV-Fast P. The solution was heated to 100 °C at a rate of 2 °C/min, and this temperature was maintained for 50 min; afterwards, the solution was cooled to 70 °C at a rate of 2 °C/min. Finally, the fabric was removed and completely washed in distilled water.

2.3 Measurements

2.3.1 Uptake of PPBC

The absorption spectra and absorbance (λ_{\max} , 244 nm) of PPBC solutions were measured using a Shimadzu UV-1800 UV-vis spectrophotometer (Shimadzu Co., Japan). According to the previously established absorbance/concentration relationship, the quantity of PPBC in solution was able to be calculated, and the percentage of exhaustion was determined using the following equation:

$$\text{Exhaustion (\%)} = \frac{m_0 - m_1}{m_0} \times 100 \quad \dots (1)$$

where m_0 and m_1 are the quantities of PPBC in solution before and after treatment, respectively. The quantity (C_f , mg/g) of the adsorption of PPBC on PLA fibre was calculated by the difference in the initial and final concentrations of PPBC in solution as well as the weight of the dried fibre.

2.3.2 Hydrophilicity

The hydrophilicity of PLA fabric was evaluated by measuring the wetting time of a water droplet on the fabric surface. In the wetting time test, a drop (0.1 mL) of distilled water from a height of 1 cm was placed on the surface of a fabric fixed evenly above a beaker. The wetting time for a drop of distilled water to sink into the sample was recorded. Each sample was measured three times, and the average value was reported.

2.3.3 Durability to Laundering

To evaluate the durability to laundering, the PLA fabric finished with 2% (owf) PPBC was laundered in a 5 g/L solution of standard synthetic detergent at 40 °C using a 30:1 liquor ratio. The laundering was performed in the sealed and conical flask immersed in the XW-ZDR low-noise oscillated dyeing machine (Jiangsu Jingjiang Xingwang Dyeing and Finishing Machinery Factory, China). Every 5 min laundering was defined as one cycle and at the end of each cycle, the fabric was rinsed thoroughly in distilled water. After different cycles of laundering, the fabric was allowed to dry in the open air.

2.3.4 Ultraviolet Protection Ability

The UV protection factor (UPF) of fabrics was evaluated in a Labsphere UV-1000F ultraviolet transmittance analyzer (Labsphere Inc., USA). Each sample was tested four times at different positions, and the average of the data was used.

2.3.5 Colour Depth

The apparent colour depth (K/S) of dyed fabrics was determined using a HunterLab UltraScan PRO reflectance spectrophotometer (illuminant D65; 10° standard observer). Each sample was folded twice so as to give a thickness of four layers.

2.3.6 Light Radiation Stability

The stability of dyed fabrics subjected to light exposure was evaluated using an Atlas XenoTest Alpha (SDL Atlas, USA) light fastness tester according to GB/T 8427-2008, and the fabrics were exposed to xenon arc lamp for 20 h under standard testing conditions. The photofading rate of dyeings was calculated using the following equation:

$$\text{Photofading rate (\%)} = \frac{(K/S)_0 - (K/S)_1}{(K/S)_0} \times 100 \quad \dots (2)$$

where $(K/S)_0$ and $(K/S)_1$ are the colour depth of fabrics before and after exposure to light respectively.

3 Results and Discussion

3.1 Hydrophilization

3.1.1 Effect of Finishing Conditions on Uptake of PPBC and Hydrophilicity of PLA

Figure 1 shows that the exhaustion of PPBC increases with increasing treatment temperature. The increasing exhaustion is due to the higher kinetic energy of PPBC molecules and the higher swelling of PLA fibre. The temperature below or equal to 100 °C is considered to be more favorable in order to avoid the high temperature degradation of PLA⁶. It has to be mentioned that PPBC exhibits much higher uptake by PLA fibre than by PET fibre. When PPBC is applied on PET fibre, its exhaustion is found to be below 10%. This indicates that PPBC has a high utilization rate when applied to the finishing of PLA. The reason is probably that the low glass transition temperature of PLA fibre^{1,13} facilitates the intercalation of the hydrophobic polyester segments of PPBC into the inner surface layer of PLA fibre.

The water absorption time of the original PLA fabric (not subjected to high temperature treatment) exceeds 300 s, revealing its poor hydrophilicity²². After finishing, PLA fabric shows the short water absorption time, which decreases with increasing treatment temperature, indicating its good hydrophilicity. What is noteworthy, however, is the wettability of the control fabric treated in pure water at 100 °C. The water absorption time of the control

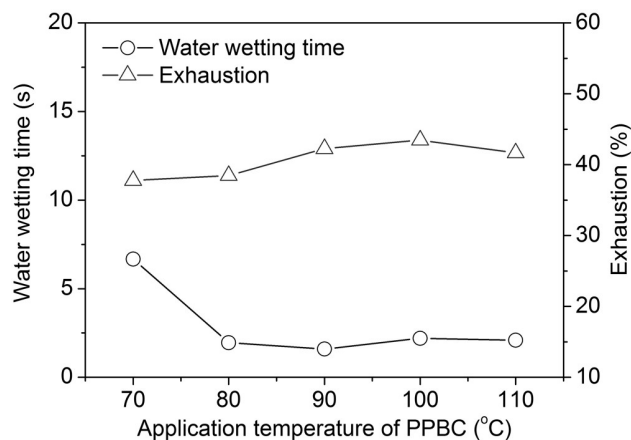


Fig. 1 — Effect of finishing temperature on exhaustion of PPBC and hydrophilicity of PLA fabric

fabric is found to be 30 s or so. This increase in hydrophilicity possibly results from the hydrolysis of PLA at high temperature which produces the hydroxyl and carboxyl groups on the PLA surface¹⁰.

Figure 2 shows that the quantity of PPBC adsorption on PLA linearly increases with increasing PPBC concentration over the limited concentration range. However, the water absorption time of PLA fabric decreases steeply at first, and then decreases gently with increasing PPBC adsorption. This suggests that there is no necessity to employ a high PPBC dosage for the good hydrophilicity of PLA fabric. A low dosage of PPBC can provide an adequate number of adsorbed PPBC molecules whose flexible polyether segments cover the hydrophobic surface of PLA fibre and make the PLA surface turn from hydrophobic to hydrophilic.

3.1.2 Effect of Finishing Temperature on Resistance of Hydrophilicity to Laundry

The laundry resistance of the hydrophilicity of the finished fabric is of great significance for practical application. Figure 3 shows the water absorption time of the PLA fabrics modified at 80 °C and 100 °C after different cycles of laundering. Apparently, the PLA fabric modified at 100 °C still displays very short water absorption time as compared to that modified at 80 °C after repeated laundering, revealing its good durability to laundering. Therefore, it is deemed that a high temperature finishing contributes to the deep intercalation of the hydrophobic polyester segments of PPBC into the inner surface layer of PLA fibre, and can enhance the laundry resistance.

3.2 Simultaneous Hydrophilization and UV Protection Finishing

Hydrophilicity and UV protection are two important properties to be necessarily upgraded for polyester textiles. Commercial UV absorbers suitable for the processing of polyester fibres are usually provided in a water-paste form, and dispersed in solution when applied. They can be adsorbed by fibres and also diffuse into fibre interior, thus behaving like disperse dyes. Hydrophilic PPBC macromolecules are also dispersed in water. From the point view of the functionalities and compatibility of chemicals, the feasibility of the integrated hydrophilization and UV protection finishing using UV absorber and PPBC is worthy of discussion.

The UV protection performance of a fabric can be characterized using UPF. Figure 4 shows the UPF values of PLA fabrics finished with UV-Fast P in the presence and absence of PPBC. The fabrics

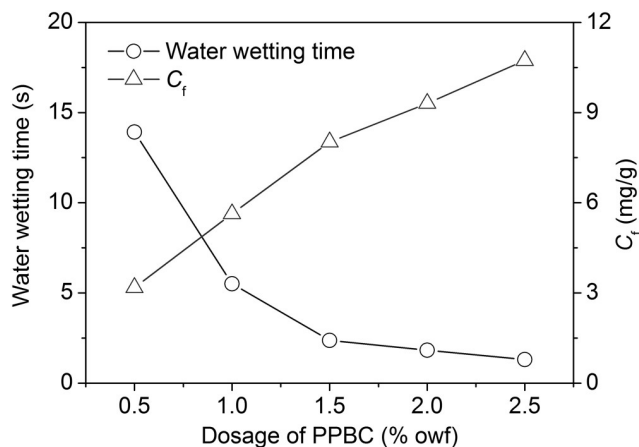


Fig. 2 — Effect of PPBC dosage on adsorption quantity of PPBC and hydrophilicity of PLA fabric

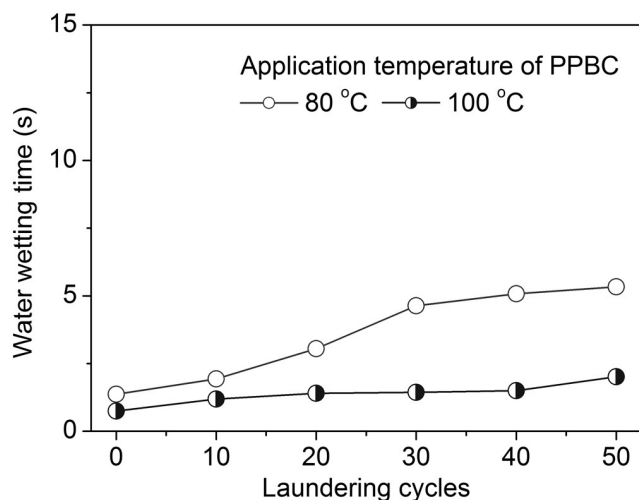


Fig. 3 — Wetting time of the finished PLA fabric after different cycles of laundering

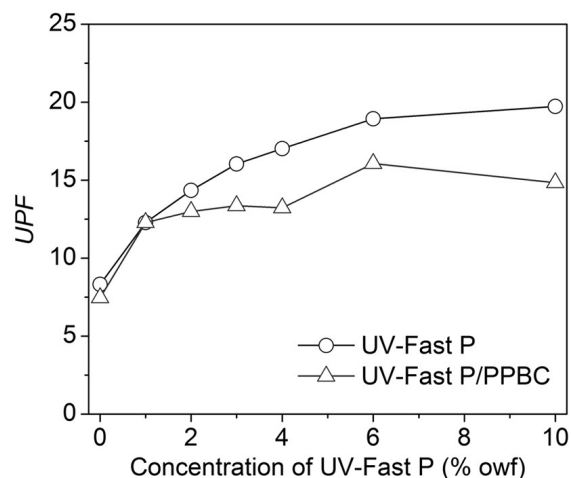


Fig. 4 — UPF values of PLA fabrics finished with UV-Fast P in the presence and absence of PPBC (2% owf PPBC and 0-10% owf UV-Fast P).

unfinished and finished with PPBC displayed low UV protection ability. Although PPBC contains aromatic moiety and has absorption in the UV region, it cannot impart UV protection effect on PLA fabric due to its low extinction coefficient. As shown in Fig. 4, the UPF values increases with increasing dosages of UV-Fast P, indicating that the treatment of a UV absorber is able to enhance the UV protection ability of PLA fabric, and that the triazine-based UV absorber has the good building-up property on PLA fabric. However, the addition of PPBC into solution decreases the UPF values of UV protection fabrics, implying that the adsorption quantity of UV-Fast P is negatively affected by PPBC. The reason for this observation might be that PPBC decreases the disperse stability of UV-Fast P, and that the distribution of PPBC on the outer and inner layers of PLA fibre obstructs the adsorption and diffusion of UV absorber molecules on PLA fibre.

In terms of hydrophilicity, both the PLA fabrics obtained by the individual PPBC finishing and the combined PPBC/UV-Fast P finishing are able to exhibit the water wetting time of 1.5–2 s. In other words, the addition of a UV absorber into PPBC solution has no impact on the hydrophilicity of PLA fabric. This also means that the water wettability of the polyether segments of PPBC distributed on the PLA surface is not affected by the UV absorber in fibre substrate. Figure 2 reveals the dependence of the hydrophilicity of PLA on the quantity of PPBC adsorption. Although the uptake of PPBC in the presence of a UV absorber is difficult to be determined spectrophotometrically, it can be preliminarily regarded that the adsorption of PPBC by PLA is less affected by the presence of a UV absorber according to nearly the same water wetting time of the PLA fabrics finished using the PPBC and PPBC/UV-Fast P treatment.

3.3 Simultaneous Dyeing, Hydrophilization and UV Protection Finishing

The one-step dyeing and finishing of PLA fabric possess the potential to save time and energy, reduce cost, and increase production and efficiency. Thus, the simultaneous dyeing, hydrophilization and UV protection finishing of PLA fabric are expected to be carried out.

Figure 5 shows that integrated dyeing and finishing slightly decreases the colour depth of the dyed PLA fabrics as compared to individual dyeing. The decrease percentage ranges from 11% to 21%,

depending on dye species. There are two possible reasons leading to this decrease, namely (i) the competitive adsorption of dyes and UV absorber on PLA fibre, and (ii) the dependence of dye adsorption on PPBC similar to the effect of PPBC on the adsorption of UV-Fast P as described above. However, this extent of decrease in colour depth can be accepted when the pale dyeing is carried out.

Disperse dyes can theoretically impart a certain degree of UV protection effect to the dyed PLA fabrics due to their UV absorption characteristics caused by the conjugated systems in their molecules. But the PLA fabrics dyed with disperse dyes exhibit slight increase in UPF (Fig. 6) as compared to the undyed PLA fabrics as indicated in Fig. 4, in the absence of UV-Fast P because the used dye

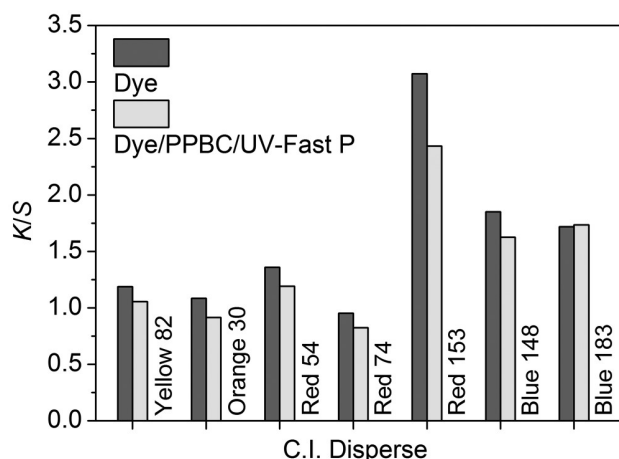


Fig. 5 — Colour depth of PLA fabrics obtained by integrated dyeing, hydrophilization and UV protection finishing (0.1% owf dyes, 2% owf PPBC and 6% owf UV-Fast P).

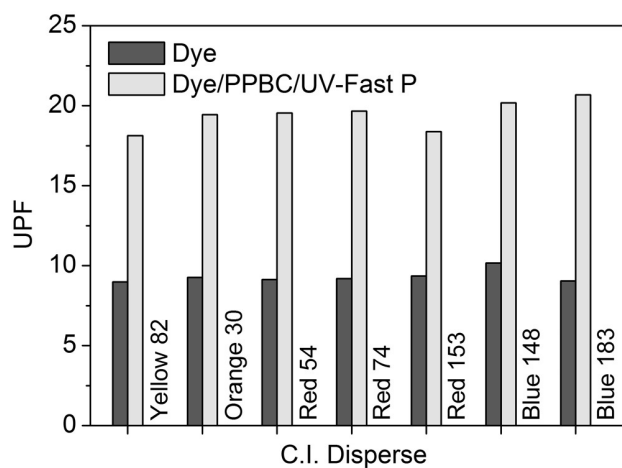


Fig. 6 — UPF values of PLA fabrics obtained by integrated dyeing, hydrophilization and UV protection finishing (0.1% owf dyes, 2% owf PPBC and 6% owf UV-Fast P).

concentration is very low. According to Fig. 6, the PLA fabrics dyed with seven disperse dyes display the average UPF value of 9.30, whereas those subjected to the integrated dyeing, hydrophilization and UV protection finishing show the average UPF of 19.43. Thus, the obviously improved UV protection effect is achieved by means of the integrated dyeing and functional finishing.

Because of the contribution of UV absorber in PLA fibre, the dyed samples exhibit better UV radiation stability (lower photofading rate). The photofading rates of the samples dyed with C.I. Red 74, Red 153 and Blue 183 using the integrated dyeing, hydrophilization and UV protection finishing are found to be 25.97%, 23.27% and 24.35% respectively, whereas those of the samples only dyed with the related dyes are found to be 18.86%, 17.27% and 18.36% respectively. The average photofading rate of the samples dyed with three dyes decreases from 24.53% to 18.16%.

It is worth pointing out that the integrated dyeing, hydrophilization and UV protection finishing can impart the good hydrophilicity to PLA fabric. The samples obtained by the integrated dyeing and finishing with different dyes are found to exhibit the water wetting time of 1.5–2.5 s.

4 Conclusion

The hydrophilic functionalization of PLA fibre is successfully achieved using a low dosage of PPBC by exhaust application. The intercalation of the hydrophobic polyester segments of PPBC into PLA fibre and the distribution of the hydrophilic polyether segments on PLA surface cause increase in hydrophilicity. A high temperature finishing increases the quantity of PPBC adsorption and the laundry resistance of hydrophilicity effect. The successful application combination of hydrophilic finishing with dyeing and UV protection treatment is able to impart the colour and functional properties to PLA fibre. This study points out that the simultaneous application of the macromolecular hydrophilic agent and the small molecular dyes and UV absorber is feasible for the wet processing of palely dyed PLA textiles, and can overcome the inherent disadvantages of PLA fibre.

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