Study on polyester fabric grafted with acrylic acid initiated by ultraviolet light

Xie Xin-Cheng, Yi Xiao-Jing, Huang Wen, Li Zuo-Shen, Ling Xin-Long* 
Guangxi University of Science and Technology, Biological and Chemical Engineering Department, Liuzhou, China
*Corresponding author: lxl29981@sina.com

Abstract. Polyester fabric has compact molecular chain structure, high crystallinity, no hydrophilic groups except hydroxyl groups at both ends, and poor hygroscopicity. The surface of polyester fabric was modified with acrylic acid by ultraviolet light in order to improve its hydrophilicity. The best technological conditions are as follows: the concentration of acrylic acid is 10%, the irradiation time is 1 hour, and the concentration of photoinitiator is 5%. Under the optimum conditions, acrylic acid is successfully grafted onto the surface of polyester fabric. There are grafting polymer between the fiber gaps or on the surface of fiber, accompanied by cross-linking or bonding. The hydrophilicity and dyeing rate of modified polyester fabric are improved obviously. The breaking strength and elongation at break of treated polyester fabric increases and decreases, respectively.

1. Introduction
Polyester fabric has become one of the most commonly used polymers in textile applications because of its excellent properties, such as good washing and wear, good dimensional stability, wrinkle resistance and rapid drying[1,2]. However, the lack of polar groups (OH, COOH, NH₂, etc.) on the macromolecular backbone of polyester fabric results in poor water absorption and hygroscopicity, which limits its application in sportswear, clothing, furniture, bedding and other textiles[2]. At present, grafting hydrophilic monomers containing carboxylic acid, hydroxyl or amide groups, such as acrylic acid, onto polyester fabric is one of the effective ways to improve the hydrophilicity of polyester fabric. The common modification techniques involve plasma treatment, corona discharge, UV/O₃ irradiation, etc[3,4]. Among these modification techniques, UV-induced surface grafting polymerization has been widely used as a simple, practical and flexible method to improve the surface properties of polymer materials[1,5].

2. Experimental

2.1 Materials
Polyester fabric was purchased from Hebei Jinzhou Dapeng Weaving Factory (China) (longitude and weft density: 55 pieces / 5 cm × 185 pieces / 5 cm). Methanol and anhydrous sodium carbonate were purchased from Guangdong Guanghua Science and Technology Co., Ltd. (China). 2959 photoinitiator was purchased from Shanghai Houcheng Fine Chemical Co., Ltd. (China). Acrylic acid was purchased from Chengdu Kelong Chemical Reagent Factory. (China). Nitric acid, dimethyl sulfoxide, sodium sulfide hexahydrate and acetone were purchased from Xilong Science Co., Ltd.(China). Methylene blue and sodium chloride were purchased from Tianjin Damao Chemical Reagent Factory (China).
2.2 Pretreatment of polyester fabric
Polyester fabric is cut to a sample of 20 cm × 20 cm. The sample was successively boiled in deionized water at 60 °C for 1 hour, and treated with ultrasonic at 25 °C in acetone for 30 minutes (bath ratio was 1:100). The treated polyester fabric was baked in an oven at 100 °C for 30 minutes.

2.3 Preparation of amino polyester fabric
The polyester fabric was immersed in nitric acid solution under stirring for 30 minutes. The treated fabric was taken out and placed at the mouth of the beaker for drying, and then placed in the oven at 80 °C for 40 minutes in order to prepare nitrified polyester fabric. The nitrified polyester fabric was washed with deionized water for three times. And then it was immersed in a mixed solution of sodium sulfide at the concentration of 39.245 g/L and sodium carbonate at the concentration of 20 g/L (bath ratio is 1:30). Lastly, treated polyester fabric was washed with deionized water and dried. The resulted polyester fabric was amino polyester fabric.

2.4 Grafting reaction of amino polyester fabric
The amino polyester fabric was placed in 2959 photoinitiator methanol solution (bath ratio is 1:30), the dipping time was 20 minutes, and then dried. The amino polyester fabric was placed in acrylic acid solution (bath ratio is 1:30) and the dipping time was 20 minutes. The samples were exposed to ultraviolet light in the darkroom for a period of time, then washed and dried. It was named unexpanded polyester fabric.

2.5 Graft reaction of expanded amino polyester fabric
A certain quality of amino polyester fabric was placed in dimethyl sulfoxide solvent according to the bath ratio of 1:30, and then it was expanded in water bath at 80 °C for 30 minutes. After expansion, the expansion agent was washed with deionized water (bath ratio of 1:100) and dried at room temperature. The expanded amino polyester fabric was modified by the method mentioned above. It was named expanded polyester fabric.

2.6 Grafting rate of polyester fabric
The grafting rate (G%) was determined by weighing the quality of polyester fabric before and after grafting. The calculation formula is as follows:

\[ G\% = \frac{W_1 - W_0}{W_0} \times 100\% \]  

Where \( W_0 \) and \( W_1 \) are the quality (g) of polyester fabric before and after grafting, respectively.

2.7 Dye uptake of polyester fabric
The dye uptake was determined according to the concentration of methylene blue in the dye solution before and after dyeing. The dye uptake formula is as follows:

\[ E = \frac{C_0 - C_1}{C_0} \times 100\% \]  

Where \( E \), \( C_0 \) and \( C_1 \) are the dye uptake, initial concentration of methylene blue solution (g/L) and concentration of methylene blue after absorption of polyester fabric (g/L), respectively.

2.8 Fabric strength test
The breaking strength and elongation of polyester fabrics were determined according to the test standard GB / T 3923-1997. The breaking strength and elongation of raw polyester fabric, amino polyester fabric, unexpanded polyester fabric and expanded polyester fabric were tested, and they were cut into 20 cm × 5 cm. The clamping length was 200 mm, the tensile speed was 100 mm / min, and the initial tensile force is 2 N. The data were recorded, and the average value of multiple measurements were taken finally.
2.9 Characterization
During the dyeing process of methylene blue solution, the sample was placed in a conical bottle, and the methylene blue solution (bath ratio is 1:50) was added to the conical bottle and heated to boiling in a constant temperature water bath. Keep boiling for 1 hour and then cool to room temperature. The hydrophilicity of the fabric was tested according to the standard AATCC 79-2010. The morphology of polyester fabric was observed by scanning electron microscope (SEM). The SEM was carried out on a QUANTAFEG450 instrument. The contact angle refers to the angle between the tangent of the solid-liquid contact interface and the tangent of the gas contact interface. When the contact angle is $0 < \theta < 90^\circ$, the polyester fabric is partially wetted, and when $\theta > 90^\circ$, the polyester fabric can not be wetted. In the meanwhile, the larger the contact angle is, the worse the wettability is. The SL150 contact angle measuring instrument produced by Solon Information Technology Company was used to measure the contact angle. The data were read when 5 μL water droplets contacted the fabric for 60 seconds, and each sample was measured at different positions for 5 times and the average value was taken.

3. Results and discussion

3.1 Effect of acrylic acid concentration on grafting rate
Fig.1 shows the effect of acrylic acid concentration on the grafting rate of amino polyester fabric. The results showed that, with the increase of acrylic acid concentration, the grafting rate increased firstly and then essentially unchanged when the concentration range of acrylic acid was 1-16%. When the acrylic acid concentration was 10%, the grafting rate of amino polyester fabric was the highest.

![Fig.1 The effect of acrylic acid concentration on the grafting rate of amino polyester fabric.](image)

3.2 Effect of irradiation time on grafting rate
Fig.2 shows the effect of irradiation time on the grafting rate of amino polyester fabric. The results showed that, with the increase of irradiation time, the grafting rate of acrylic acid on amino polyester fabric increased at first and then remained unchanged. When the irradiation time was 60 min, the grafting rate of amino polyester fabric was the highest.

![Fig.2 The effect of irradiation time on the grafting rate of amino polyester fabric.](image)
Fig. 2 The effect of irradiation time on the grafting rate of amino polyester fabric.

3.3 Effect of photoinitiator concentration on grafting rate

Fig. 3 shows the effect of photoinitiator concentration on the grafting rate of amino polyester fabric. The results showed that the grafting rate of amino polyester fabric increased at first and then decreased with the increase of photoinitiator concentration. When the concentration of photoinitiator was 5%, the grafting rate of amino polyester fabric was the highest.

Fig. 3 The effect of photoinitiator concentration on the grafting rate of amino polyester fabric.

3.4 Methylene blue dye-uptake

Table 1 shows the dye-uptake of polyester before and after grafting acrylic acid. The results showed that the dye-uptake of raw polyester fabric with methylene blue was only 3.59%, and the dye-uptake of amino polyester fabric was 8.54% which showed the amino groups on polyester fabrics had an affinity for dyes. The dye-uptake of polyester fabric grafted with acrylic acid increased obviously, and the dye-uptake of unexpanded polyester fabric and expanded polyester fabric reached 57.96% and 57.98%, respectively. This is ascribed to the introduction of hydrophilic carboxyl groups on the surface of amino polyester fabric, which has affinity for water-soluble dye methylene blue.
Table 1. The dye-uptake of polyester fabric.

| Sample                        | Dye uptake(%) |
|-------------------------------|---------------|
| Raw polyester fabric         | 3.59          |
| Amino polyester fabric       | 8.54          |
| Unexpanded polyester fabric  | 57.96         |
| Expanded polyester fabric    | 57.98         |

3.5 Hydrophilicity of polyester fabric

Table 2 shows the hydrophilicity of polyester fabrics before and after grafting acrylic acid. It is shown that the water droplets cannot be absorbed within 20 min on the surface of raw polyester fabric, and the water droplets on the surface of the modified polyester fabric can be absorbed in a short time. The water drop absorption times of amino polyester fabric, unexpanded polyester fabric and expanded polyester fabric are 12.6, 2.52 and 1.68 min, respectively. It can be seen that the hydrophilicity of polyester fabric grafted with acrylic acid by ultraviolet irradiation has been obviously improved.

Table 2. Hydrophilicity of polyester fabrics before and after grafting acrylic acid.

| Sample                        | Time (min) |
|-------------------------------|------------|
| Raw polyester fabric         | >20        |
| Amino polyester fabric       | 12.6       |
| Unexpanded polyester fabric  | 2.52       |
| Expanded polyester fabric    | 1.68       |

3.6 Electron microscope photos of polyester fabric

Figure 4 shows the electron microscope photos of polyester fabric before and after grafting acrylic acid. Before treatment, the surface of polyester fabric is smooth and glossy, the gap between fibers is large, and the arrangement is loose (Fig. 4 (a), (b)). After treatment, there are grafting polymer between the gaps of polyester fabric, and the fiber spacing becomes smaller, accompanied by cross-linking and bonding, and the luster decreases (Fig. 4 (c), (d)).
Fig. 4 Electron microscope photos of polyester fabric before and after grafting acrylic acid. (a) raw polyester fabric, (b) amino polyester fabric, (c) unexpanded polyester fabric, (d) expanded polyester fabric.

3.7 Contact angle of polyester fabric

Figure 5 shows the contact angle of polyester fabric before and after grafting acrylic acid. It can be seen from Table 3 that the contact angles between the surface of raw polyester fabric and amino polyester fabric are both more than 90 °, and water droplets form beads on their surface (figure 5 (a), (b)). Polyester fabric can not be wetted and shows hydrophobicity. However, the contact angle of treated polyester fabric are both less than 90 °, most of the water droplets permeate into the polyester fabric, and the hydrophilicity is obviously good (figure 5 (c), (d)).

Table 3. The contact angles of polyester fabrics.

| Sample                        | Contact angle(°) |
|-------------------------------|------------------|
| Raw polyester fabric          | 124.49           |
| Amino polyester fabric        | 105.99           |
| Unexpanded polyester fabric   | 48               |
| Expanded polyester fabric     | 47               |
3.8 Mechanical properties of polyester fabric

Table 4 shows the mechanical properties of polyester fabric before and after grafting acrylic acid. The breaking strength and elongation at break of raw polyester fabric are 666.37 N and 12.66%. Compared with the mechanical properties of raw polyester fabric, the mechanical properties of amino polyester fabric changed little. They are 674.36 N and 13.07%, respectively. But the mechanical properties of unexpanded polyester fabric and expanded polyester fabric are different from those of raw polyester fabric. The breaking strength and elongation at break of unexpanded polyester fabric are 471.29 N and 16.34%, and those of expanded polyester fabric are 449.38 N and 16.20%. This is ascribed to the effect of UV irradiation on PET fabric which is very obvious. The molecular chain of polyester fabric is broken and its molecular weight is reduced, which leads to the decrease of mechanical breaking strength and the increase of elongation at break.

| Sample                   | Breaking strength (N) | Elongation at break (%) |
|--------------------------|-----------------------|-------------------------|
| Raw polyester fabric     | 666.37                | 12.66                   |
| Amino polyester fabric   | 674.36                | 13.07                   |
| Unexpanded polyester fabric | 471.29            | 16.34                   |
| Expanded polyester fabric | 449.38              | 16.20                   |

4. Conclusions

Polyester fabric has compact molecular chain structure, high crystallinity and poor hygroscopicity. The surface of polyester fabric was modified with acrylic acid by ultraviolet light. When the concentration of acrylic acid is 10%, the illumination time is 1 hour, and the concentration of photoinitiator is 5%, the grafting rate of polyester fabric is the highest. Under the optimum conditions, acrylic acid was
successfully grafted onto the surface of polyester fabric. There are grafting polymer between the fiber and the fiber, accompanied by cross-linking and bonding. The modified polyester fabric can absorb the water droplets on its surface in a short time, and the contact angle is less than 90°. The hydrophilicity and dye-uptake of polyester fabric after treatment were improved obviously. Meanwhile, the breaking strength and elongation at break of treated polyester fabric increases and decreases, respectively.

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