Influence of cationization PAMAM on the dyeing property of viscose fiber

Abstract
The viscose fibers were modified by Polyamidoamine (PAMAM) which was one kind of cationic modifier in proportion with wet spinning. The surface morphological and chemical properties of modified viscose fibers were characterized by Fourier transform infrared spectroscopy (FTIR) and Scanning electron microscope (SEM). The dyeing property and adsorption isotherm of the modified viscose fiber with active dark blue K-R were investigated. The washing fastness, breaking strength and hygroscopic performance were carried out at a constant temperature.

The research results show that the physical structure and chemical properties of the viscose modified by a little amount of PAMAM were not affected. With the increasing of the amount of PAMAM increased in viscose fiber, the main adsorption and dyeing mechanism of viscose fiber has been changed from Freundlich-type physical non-localized adsorption to Langmuir-type chemical localized adsorption. The breaking strength and washing fastness of viscose fiber has no effect on with the addition of PAMAM. The cationic modifier PAMAM can increase the dyeing rate and percentage of dyeing of viscose fiber, which is of great significance for improving viscose fiber dyeing process.

Keywords: viscose fiber, PAMAM, active dyes, dyeing thermodynamics

Introduction
Viscose fibers as one kind of regenerated cellulose fibers with very good take-up and dyeing vividness properties are widely used in various industries. Due to the increasing awareness of environmental protection among today, the green and pollution-free printing and dyeing process will be an inevitable trend in the development of textiles.1−3 The dyeing of viscose fiber by reactive dyes requires the addition of a large amount of inorganic salts to promote dyeing, which will have a serious impact on the environment.4−5 Many new techniques have been studied to improve the dyeing properties of reactive dyes, such as Cold-rolled pile process, electrochemical dyeing and fiber surface modification. Cold-rolled pile process and electrochemical salt-free dyeing can significantly improve the dyeing rate and reduce wastewater discharge.6−10 However, they separately need to spend more dyeing time and be equipped with special electrochemical devices, which are difficult for industrial continuous production. The introduction of a cationic group on the surface of the fiber can be absorbed by the anion of the reactive dye, which is advantageous for improving the fixing rate of the reactive dye under low-salt or salt-free conditions.11 Cationic Modifier M is a Gemini type surfactant containing two alkyl groups and quaternary ammonium salts.12 After modification, the fabric is coated with quaternary ammonium salt positive ions, so that the dye uptake rate and fixation rate are similar to conventional dyeing, and the salt dosage can be dramatically drop. The cationic modifier 3-methacryloyl amino propyl trimethyl ammonium chloride (MAPTAC) can improve the dye uptake, surface color and color fastness of reactive dyes, which is higher than traditional dyeing.13 After the fabric is modified by polyepichlorohydrin and dimethylamine (PECH-A), the fixing dye can reach 90% or more under salt-free conditions.14 When the same color depth is achieved, the modified fabric can save more than 80% of the dye. However, fiber surface modification requires the adsorption of cationic groups on the surface of the fiber, which undoubtedly increases the cost of industrial production.

The Polyamide-amine (PAMAM) consists of an initial initiation nucleus, a repeating branching inner layer structure and a surface functional group, and the macromolecular compound having a large number of terminal functional groups is formed by the initial initiation of the nucleus expanding outward through the branching unit.15−17 The size, shape, and surface functional groups of PAMAM are controllable, with good hydrodynamic properties, unique viscosity properties, easy film formation properties, good reaction properties, unique refractive index increments, unique surface activity and good solubility, these unique properties are widely used in dyeing18 and functional finishing.19 The PAMAM has not yet been applied to viscose fibers to improve dyeing efficiency and reduce energy consumption.

The purpose of this study was to investigate the influence of PAMAM on the dyeing properties of the viscose with wet-spinning. Surface morphology and chemical composition were analyzed by SEM and FTIR. The PAMAM modified viscose fiber was dyed with active dark blue K-R to investigate their dyeing and thermodynamic properties. The physical properties of the PAMAM modified viscose fiber were analyzed by washing fastness and breaking strength.

Experimental
Materials and chemicals
Fiber: Self-made viscose fiber and modified viscose fiber containing 6%, 8% and 10% PAMAM.
Dye: Active Dark Blue K-R (Refined, Jinan Baoda Dye Co., Ltd, China) (Figure 1).
Additives: Anhydrous sodium carbonate (Analytical Pure, Tianjin Dingshengxin Co., Ltd, China).
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The adsorption isotherm is calculated according to formula (1).

\[ C = \frac{G_b - G}{G} \times 100\% \]  

(1)

Dyeing thermodynamic test of viscose fiber

Preparation of standard dye solution: The dye was accurately weighed 0.2g and dissolved in distilled water with a 100mL beaker, the dyeing liquid was diluted with an 1000mL volumetric flask.

Drawing of adsorption isotherms: The 0.4g/L standard dye solution was taken into 8 dye cups by respectively taking 1, 2, 3, 4, 5, 6, 7 and 8ml. The cup is added with buffer to make the volume of the dye solution 200ml, so that 8 kinds of dye solutions with different mass concentrations could be obtained. The dye solution was preheated to 60°C, and the equal amount of fiber was respectively put in 8 dye cups at the same time (fiber quality is 1g, so the dye bath ratio is 200: 1). The dyeing cup was placed in a constant temperature water bath with a temperature of 60°C, and the constant temperature water bath was quickly adjusted to 90°C, and the dye cup was insulated for 10h. After dyeing, the fiber samples in the dyeing cup were picked and washed. Then the washing solution was poured into a volumetric flask, and the volumetric flask was brought to a volume of 250ml. Finally, the absorbance is measured separately to draw the adsorption isotherm.

Judgment of adsorption isotherm: The adsorption isotherm is a relationship between the concentration of the dye dyed onto the fiber and the concentration of the remaining dye in the dye liquor at a constant temperature, when the dyeing reaches equilibrium. Its significance has the following two points: First, according to the distribution relationship of the dye on the fiber and the concentration in the dyeing solution after the dyeing reaches equilibrium, the dyeing ability and the dye utilization rate can be known when the dye concentration is different; The adsorption dyeing mechanism of the dye is derived from the adsorption isotherm, and the affinity of the non-ionic dye is calculated. For the ionic dye, the affinity cannot be directly calculated by the adsorption isotherm. Generally, the shape of the adsorption isotherm has a certain relationship with the structure of the dyed fiber, the dye structure, the dye variety, and the dyeing conditions. There are three main types of dye-to-fiber adsorption isotherms: Nernst, Langmuir and Freundlich.[21,22]

Determination of wash fastness

The test standards for wash fastness are carried out in accordance with the relevant provisions of GBT 8629-2017 “Textile testing Household washing and drying procedures”. The specific operation steps are as follows: firstly, a number of single-fiber lining-like adhesives and cotton are cut out, the specification is 40×100mm; the fiber and the lining are stitched along the four sides; secondly, a soap bath having a bath ratio of 1:50 was prepared, which contained 5g/L of soap powder and 2g/L of sodium carbonate. The fabric was taken out of water and dried after soaped for 30min. Then the color change and staining were evaluated according to the standard GB/T8424.1-2001.

Viscose fiber strength

The mechanical properties of the modified viscose fiber before and after dyeing were tested by LLY-06E electronic single fiber strength meter. The experimental results were averaged after 20 tests and the experimental conditions were as follows: the temperature was 20°C,
the humidity was 65%, the gauge was 10mm, and the tensile rate was 10mm/min.

**Result and discussion**

**Scanning electron microscope**

The unmodified viscose fiber and the PAMAM modified viscose fiber were observed by scanning electron microscope, and the results are shown in Figure 2. It can be seen that the modified viscose fiber has a uniform thickness; It can also be found that the self-made fiber has a straight groove, which is the same as ordinary viscose fiber,21 indicating the addition of PAMAM to viscose fiber has little effect on the surface morphology of viscose fiber. The radius of the viscose fiber and the PAMAM modified viscose fiber are very similar, indicating that PAMAM has no significant influence on the thickness of the viscose fiber.

**Infrared spectrum**

Infrared spectral scanning of viscose fiber and modified viscose fiber by KBr tableting. It can be seen from Figure 3 that the modified viscose fiber has a larger hydroxyl absorption peak at 3306.77cm\(^{-1}\), which is mainly due to the fact that the end group of the PAMAM is an amine group, and the stretching vibration of N-H overlaps with the stretching vibration peak of the hydroxyl group. The peaks were found to be large at 1645.11cm\(^{-1}\), 1357.14cm\(^{-1}\) and 1315.19cm\(^{-1}\), indicating that the amides I and II in the PAMAM overlap with the six-membered C-C absorption peaks in the viscose fibers. The \(-\text{CH}_2-\) vibration absorption peak appearing at 2878.95cm\(^{-1}\) and the stretching vibration absorption peak of tertiary amine appearing at 1010cm\(^{-1}\) have become larger, indicating that the PAMAM enters the inside of the fiber.

**Hygroscopic performance**

Hygroscopicity is one of the indicators of the physical properties of fibers. Hygroscopicity refers to the ability to absorb water from a gaseous environment. The experimental results are shown in Table 1. It can be seen that the adsorption capacity of the PAMAM modified viscose fiber for different liquids is that the physiological saline is larger than the distilled water; for the same solution, the adsorption capacity of the modified viscose fiber is enhanced with the increase of the PAMAM addition amount. The aspiration of modified viscose fiber to physiological saline is due to the reaction of anion (Cl\(^-\)) in the physiological saline and the terminal amino group of the PAMAM.

| Fiber samples | Aspirate C(g/g fiber) | Distilled water | Saline |
|---------------|-----------------------|-----------------|--------|
| 0%PAMAM       | 1.12                  | 4.26            |
| 6%PAMAM       | 1.27                  | 4.83            |
| 8%PAMAM       | 1.31                  | 5.04            |
| 10%PAMAM      | 1.37                  | 5.25            |

In order to more accurately determine the adsorption isotherm type, each adsorption isotherm data is linearly fitted, \(1/D\) and \(1/D\), are in a straight line relationship, \(1/[D]\), and \(1/[D]\) are in a straight line relationship, \(lg[D]_r\) and \(lg[D]_r\) are in a straight line relationship. The result is shown in Figures 5–7.

The closer the linear fit \(S^2\) of the adsorption isotherm is to 1, indicating that the linear relationship is better, the more consistent with the type of adsorption isotherm. The fitting results after fitting the adsorption isotherms are shown in Table 2.
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Table 2 Fitting of each adsorption isotherm

| Types           | Straight line fit $S^2$ |
|-----------------|-------------------------|
| $[D]$           | 0.86701                 |
| 0% PAMAM        | 0.88464                 |
| 8% PAMAM        | 0.89197                 |
| 10% PAMAM       | 0.87144                 |
| $1/[D]$         | 0.92613                 |
| 0% PAMAM        | 0.99447                 |
| 8% PAMAM        | 0.99562                 |
| 10% PAMAM       | 0.99322                 |
| $\ln[D]$        | 0.9694                  |
| 0% PAMAM        | 0.9549                  |
| 8% PAMAM        | 0.96253                 |
| 10% PAMAM       | 0.96044                 |

It can be seen from Table 2 that the modified viscose fiber has different PAMAM content, and the fitted adsorption isotherms have different values. The linear fit $S^2$ of the adsorption isotherm is closer to 1, indicating that the linear relationship is better, the more consistent with the type of adsorption isotherm. The fitting results of the adsorption isotherms are shown in Table 1. The adsorption isotherm of the modified viscose fiber is closer to the Langmuir type, indicating that the modified viscose fiber is mainly chemically adsorbed by reactive dyeing. During the dyeing process, the dye concentration $[D]$ in the solution increases. The dye concentration $[D]$ on the fiber will also increase. When the dye concentration $[D]$ in the solution reaches a certain value, the dye concentration $[D]$ on the fiber will increase to a small extent, which is almost negligible. After the change of $\ln[D]$, it was found that the adsorption isotherms of the unmodified viscose fiber were in accordance with the Freundlich type, indicating that the dyeing mechanism of the unmodified viscose fiber is physical non-local adsorption. As the dye concentration $[D]$ in the solution increases, the dye concentration $[D]$ on the fiber will gradually increase, while the growth rate gradually decreases. Therefore, the main adsorption and dyeing mechanism of PAMAM modified viscose fiber on reactive dyes has changed, from Freundlich-type physical non-localized adsorption to Langmuir-type chemical localization adsorption.

Wash fastness

Color fastness refers to the resistance of the color of the textile to various effects during processing and use. The fastness level was evaluated based on the discoloration of the sample and the staining of the lining fabric. Textile color fastness test is a routine test item in textile intrinsic quality test, and its measurement is shown in Table 3.
The results show that the modification of viscose fiber does not affect the adhesion fastness of dyes and viscose fibers. After dyeing with reactive dyes, there was no significant change in fading fastness and wash fastness index.

**Breaking strength**

The breaking strength of the active dark blue K-R before and after dyeing of the modified viscose fiber is shown in Table 4.

**Table 4** The breaking strength of viscose fiber before and after dyeing with active dark blue K-R

| Fiber sample         | Breaking strength (cN/dtex) | Grade |
|----------------------|----------------------------|-------|
|                      | Pre-dyeing sample          | Dyed sample |
| Viscose fiber        | 2.35                       | 2.13  |
| Modified viscose fiber | 2.24                      | 2.06  |

It can be seen from Table 4 that the breaking strength of the PAMAM modified viscose fiber is not much different from the breaking strength of the pure viscose fiber, indicating that the addition of 10% PAMAM has a certain influence on the breaking strength of the viscose fiber, but the effect is not large. The reason may be that the PAMAM structure is fixed and open in the plane, and the molecular fiber is tightly entangled, resulting in a significant decrease in the strength of the 10% PAMAM modified viscose fiber. The active dark blue K-R is used to the modified viscose fiber, which will result in loss of fiber strength, but the effect is not significant. The reason may be that after the modified viscose fiber is dyed with reactive dye, the modified viscose fiber is contacted with air during the drying process, and the oxygen in the air oxidizes the fiber, eventually the strength of the modified viscose fiber is reduced.

**Conclusion**

The dyeing and absorption of viscose fibers modified by PAMAM in proportion with wet spinning were investigated. The method of adding PAMAM to the spinning dope can modify the viscose fiber and have less influence on the appearance and size of the fiber. The PAMAM modified viscose fiber was dyed with active dark blue K-R and compared with viscose fiber. The adsorption and dyeing mechanism of PAMAM modified viscose fiber indicates: the main adsorption and dyeing mechanism has been changed from Freundlich-type physical non-localized adsorption to Langmuir-type chemical localized adsorption, when a certain amount of PAMAM is added to the viscose fiber. It was worth to mentioning that the PAMAM modified viscose fiber has little effect on the water washing fastness and fiber strength after being dyed by reactive dyes. Therefore, this novel and easy method may bring a promising and green strategy to reduce the amount of salt used in functional textiles.

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**Conflict of interest**

Author declares there is no conflict of interest in publishing the article.

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