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Synthesis of a novel water-soluble polymeric UV-absorber for cotton

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Abstract

A water-soluble polymeric UV-absorber with polyvinylamine as backbone and benzotriazole type UV absorber as anti-UV functional group was synthesized by grafting brominated (2'-acetoxy-5'-methylphenyl)-2*H*-benzotriazole onto polyvinylamine. The intermediates and synthesized polymeric UV absorber were characterized by ¹H NMR, MS, IR and UV spectroscopy. The finishing properties of the polymeric UV absorber on cotton were investigated to show good UV protection property and wash fastness.

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Keywords: Polymeric UV-absorber; Finishing; Cotton; UV protection property

Due to ozone depletion, incidence of skin cancer has been progressively increased because of excess exposure to ultraviolet UV radiation from the sun [1]. Finishing of clothes with UV absorbers is an effective way to protect skin [2,3]. Among them, finishing of cotton fibers has been intensively studied due to their poor UV protection property [4,5]. However, most of the UV absorbers currently researched were water insoluble [6–8], they needed to be emulsified or dispersed in water and organic solvents were usually added when they were applied. Moreover, it was found that the fastness properties of some UV absorbers were not good due to non-covalent bonding between the UV absorbers and cotton. In recent years, some water-soluble reactive UV absorbers containing sulfonic acid groups were synthesized and applied to cotton [9–12]. However, the utilization ratio of the UV absorbers was low. In addition, as a large amount of inorganic salt was added to promote adsorption of the UV absorbers on cotton, serious environmental pollution was arose due to release of effluent containing salt.

In order to prepare UV absorber with water solubility, high affinity to cotton, satisfactory fastness properties together with good UV protection property, we designed a novel polymeric UV absorber by grafting benzotriazole type UV absorber onto polyvinylamine (PVAm). As PVAm shows good water-solubility and cationic properties under wide range of pH, the obtained polymeric UV absorber can be provided water-solubility and high affinity to cotton fibers through adjusting of the grafting ratio of UV absorbing component. In this study, PVAm with amination degree of 80% was synthesized from polyacrylamide by Hoffman degradation reaction [13]. 2-(2'-Hydroxy-5'-methylphenyl-2*H*-benzotriazole (UV-P), which is an excellent UV absorber in industry was used as UV absorbing component to graft onto PVAm. As more than one UV absorbing components are connected within one molecule, the anti-UV property of

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Scheme 1. Synthesis of the polymeric UV absorber.

the polymeric UV absorber would be good. In addition, after being finished on cotton, the polymeric UV absorber could be further crosslinked with cotton fibers to improve its fastness properties.

The synthesis of polymeric UV-absorber **c** is shown in Scheme 1. Compound 2-(2'-acetoxy-5'-methylphenyl)-2*H*-benzotriazole **a** was synthesized through protection of hydroxyl group of UV-P, and then hydrogen of benzyl group of **a** was brominated to get 2-(2'-acetoxy-5'-bromomethylphenyl)-2*H*-benzotriazole **b**. Amination of **b** with PVAm and deprotection of hydroxyl group of **b** were carried out at the same time to obtain product **c** under alkaline and high temperature conditions. The yield of **a** (mp 104–106 °C), **b** (mp 126–128 °C) and **c** was 95.1%, 60% and 99.0%, respectively. Agilent 8453 UV-vis spectrophotometer, FT-IR 430 spectrophotometer, HP1100 mass spectrometer and Varian Inova 400 NMR were used to determine the structures of the intermediates and the polymeric UV absorber.

¹H NMR (400 MHz, CDCl₃) data of **a** were as follows: δ 2.30 (s, 3H), 2.46 (s, 3H), 7.19 (d, 1H, J = 8.28 Hz), 7.31 (d, 1H, J = 7.78 Hz), 7.43 (dd, 2H, J = 6.53, 3.01 Hz), 7.92 (dd, 2H, J = 6.78, 3.01 Hz), 7.95 (s, 1H). MS m/z of **a** was at 290 [M+Na]⁺. FTIR (KBr) v: 1758 cm⁻¹ (stretching vibration of C=O), 1610, 1508 cm⁻¹ (skeleton vibration of benzene ring C=C), 1371 cm⁻¹ (deformation vibration of C–H of CH₃), 1226, 1206, 1190 cm⁻¹ (stretching vibration of C–O–C), and 743 cm⁻¹ (deformation vibration of C–H of benzotriazole ring). UV–vis: λ_{max} = 310 nm.

¹H NMR (400 MHz, CDCl₃) data of **b** were: δ 2.33 (s, 3H), 4.57 (s, 2H), 7.29 (d, 1H, J = 8.28 Hz), 7.44 (dd, 2H, J = 6.78, 2.76 Hz), 7.54 (d, 1H, J = 8.28 Hz), 7.92 (dd, 2H, J = 6.53, 2.76 Hz), 8.22 (s, 1H). MS m/z data of **b** was: 346 [M+H]⁺, 348 [M+H+2]⁺, 368 [M+Na]⁺, 370 [M+Na+2]⁺, and the peak intensity ratios (M+H):(M+H+2) and (M+Na): (M+Na+2) were both 1:1, which demonstrated one bromine existing in **b**. FT-IR(KBr) ν : 1754 cm⁻¹ (stretching vibration of C=O), 1610, 1507 cm⁻¹ (skeleton vibration of benzene ring C=C), 1368 cm⁻¹ (deformation vibration C–H of CH₃), 1215 cm⁻¹ (stretching vibration of C–O–C), 740 cm⁻¹ (deformation vibration of C–H of benzotriazole ring), and 648, 638 cm⁻¹ (stretching vibration of C–Br). UV–vis: $\lambda_{max} = 302$ nm.

The target compound **c** with grafting ratio of 30% of the amino group of PVAm was characterized by TLC, FT-IR and UV–vis spectra. TLC of **b** and **c** was made with dichloromethane as developer. R_f of **b** is 0.65, while that of the grafting product **c** is zero, which demonstrates that **b** has been grafted onto PVAm. FT-IR (KBr) data of **c** were as follows: 3421 cm⁻¹ (stretching vibration of N–H), 2943 cm⁻¹ (stretching vibration of NH₃⁺), 1638 cm⁻¹ (asymmetric deformation vibration of NH₃⁺), 1517 cm⁻¹ (symmetric deformation vibration of NH₃⁺), 746 cm⁻¹ (deformation vibration of =C–H in aromatic ring).

It was observed from the UV spectrum of \mathbf{c} (Fig. 1) that the characteristic absorption peaks of *o*-hydroxyphenylbenzotriazole UV-absorbers appeared at 300 nm and 332 nm, which also showed that that UV-absorber had been grafted onto PVAm. In addition, appearance of the peak at 332 nm in UV spectrum of \mathbf{c} proved the deprotection of the hydroxyl group of the UV absorbing component.

As benzotriazole group was water insoluble, with the increase of the grafting ratio of it, the water solubility of **c** decreased gradually. It showed when the grafting ratio was 30.0%, the solubility of the polymeric UV absorber **c** was still good. However, when the grafting ratio increased to 38.5%, **c** was difficult to dissolve in water. In the study, the polymeric UV absorber **c** with grafting ratio of 30% was applied to finishing of cotton fibers through exhaust method.



Fig. 1. UV spectrum of compound c.

The exhaustion ratio of the UV absorber on cotton could reach 98% when 3% (o.w.f) of the absorber was used. Crosslinking agent 2-chloro-4,6-di(aminobenzene-4'- β -sulfatoethylsulfone)-1,3,5-s-triazine DAST [14] was further padded on the cotton pretreated with the UV absorber to improve the fastness properties of the UV absorber. UPF value of the finished cotton reached 30 according to AS/NZS 4399:1996 and the wash fastness of the UV absorber was excellent according to AATCC 124-2006 after 25 cycle washing. The prepared polymeric UV absorber not only exhibited water solubility and good anti-UV property, it also showed very high utilization efficiency, satisfactory wash fastness and environmentally benign finishing process. These advantages supplied this polymeric UV absorber with promising in application.

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